Published Monthly. Price, $5.00 per Annum.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

VOL. XVIII.—NO. 4.

APRIL, 1896.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
COMMITTEE ON PAPERS AND PUBLICATIONS.

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EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

Issued with April Number, 1896.

Proceedings.

COUNCIL.

The Council have approved the nomination of Edward Hart as Editor for 1896.

CHANGES OF ADDRESS.

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ADDRESSES WANTED.

Bachman, Irving A., formerly of Augusta, Ga.
Jones, Dr. Walter, formerly of Lafayette, Ind.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The annual meeting was held January 9, 1896, and was called to order by the President, Charles E. Munroe, at 8:00 P. M.

The following persons were elected to membership: Messrs. E. W. Magruder, C. C. Moore, and E. C. Wilson.

The publication of Bulletin No. 9 was announced and arrangements reported by a committe for a social meeting to be held in February.

The reports of the Treasurer and Secretary were read and adopted, after which the election of officers for the ensuing year was held with the following result:

President—E. A. de Schweinitz.

Vice-Presidents—W. D. Bigelow and W. G. Brown.

Treasurer—W. P. Cutter.

Secretary—A. C. Peale.

Additional Members of the Executive Committee—Charles E. Munroe, V. K. Chesnut, F. P. Dewey, and H. N. Stokes.

The first paper of the evening was read by H. W. Wiley on a "Steam-Jacketed Drying Oven." "In order to surround the drying space of an oven entirely with steam, the door of an ordinary steam-jacketed drying oven is made with double walls, into which the steam from the oven is conducted by two metal flexible tubes inserted at the top and bottom of the door. They are so arranged as not to interfere with opening the door. By this method the entire drying space of the apparatus is surrounded with steam, easily securing a constant and even temperature.

"The temperature is regulated by a pressure gauge in which the steam, by acting on a column of mercury, cuts off the gas when a given pressure is reached. A steam pressure of two inches will cause a temperature of about 102° in the drying space of the oven. By setting the gauge at any position desired, the temperature can be regulated, when steam is used, to read from the boiling-point of water up to 105°. For other temperatures other liquids can be used. For instance, alcohol, or amyl alcohol for still higher temperatures, and so on. Ether cannot be employed with safety on account of the danger of explosion in case of leakage."

Dr. Wiley exhibited the drying oven in actual operation.

The second paper, also by Dr. Wiley, was on the "Heat of Bromination of Oils." "The method of determining the heat of bromination of oils, as proposed by Hehner and Mitchell, in a recent number of the *Analyst*, is very difficult to work from the meager directions given by the authors. The especial difficulty in the process is in handling the liquid bromine in quantities of one cc. at a time. I find that the process is made practicable by dissolving both the oil or fat and the bromine in chloroform, in which condition the bromine solution is easily handled by means of a special pipette.

"In order to make a number of analyses of the same sample, five grams of the fat may be dissolved in chloroform and the volume completed to fifty cc. Ten cc. of this solution will contain one gram of the fat. In like manner five cc. of bromine may be dissolved in chloroform and the volume completed to fifty cc., or larger quantities in the same proportion may be used. The

gradual evolution of hydrobromic acid from a mixture does not interfere with the analytical process, as the amount of bromine used is always largely in excess. Ten cc. of the bromine solution containing one cc. of the liquid bromine are used for each ten cc. of fat solution.

"The pipette for handling the bromine solution is so arranged as to be filled by the pressure of a rubber bulb, thus avoiding the danger of sucking the bromine vapor into the mouth. The solution is poured upon the chloroform solution held in a long narrow tube, in which a delicate thermometer, capable of being read to tenths of a degree, by means of a magnifying glass, is placed. This tube is held in a large cylinder, from which the air can be removed, thus affording a good insulation in respect to heat.

"The determinations should be conducted in a room where the temperature is as constant as possible and the pieces of the apparatus should be exposed to the open air for at least half an hour after completing one determination before beginning another, in order to be restored to the standard room temperature. Duplicates usually agree within one or two-tenths of a degree, though sometimes the variations are greater.

"The ratio of the heat of bromination to the ordinary number must be established for each system of apparatus employed. The heat of bromination of various oils was determined by the method and apparatus described above, and the process seems to be one of considerable analytical value. For exact scientific purposes, calorimetric measurements of the degree of heat produced must be made."

Discussion was by Messrs. Warder, Freeman, and Munroe.

Professor Charles E. Munroe then made some remarks upon the "Corrosion of Electric Mains." He exhibited sections of electric light cables in which the lead coating had become so corroded that in some places the interior conductor was exposed, while at others the cable was coated with nodular earthy-looking masses. The cables were parts of and arranged on the three wire system, which carried a direct current of 110 volts on each wire, and which had been laid underground in the upper compartment of a terra cotta conduit. The corroded main was a branch in an alley. The principal main in the street was not

attacked in the least. Analysis showed the incrustation to contain nitrate, chloride, carbonate, oxide of lead, water, and a trace of organic matter. Surrounding the alley were stables, and the author found in the salts in the soil produced by the excreta all the necessary materials and conditions for effecting chemical corrosion *per se*, without resorting to any electrolytic theory.

Dr. Wiley, in discussing the paper, said he thought there might have been a denitrifying process.

Professor Munroe said there could have been no constant moisture present, that is, there was no submergence, but there must have been water passing through the conduit.

CINCINNATI SECTION.

The section met in regular session Saturday evening, February 15, 1896. Vice-President Martin presided.

Dr. Alfred Springer read a paper on "The Characteristics of Illuminates," and exhibited a photograph of the bones of the hand made by means of the Roentgen X rays. The picture was kindly loaned for the purpose by Mr. G. W. Zwick, of Covington, Ky., who had recently brought it from Germany.

"Notes on Helium and Argon" was read by Professor T. H. Norton.

Dr. S. Waldbott showed how the value of litmus paper as an indicator could be enhanced. His method was to use a capillary pipette instead of an ordinary stirring rod, and to hold the point of the pipette containing a drop of the solution upon the litmus paper; a bright red spot would be seen at the point of contact, even in very dilute acid solutions. The Doctor's paper on "The Assay of Ipecac," announced for the evening, was postponed till next meeting.

NORTH CAROLINA SECTION.

On February 22nd about a dozen chemists met in the office of the Experiment Station in Raleigh to organize the North Carolina Section. The following officers were elected:

President—F. P. Venable, University of North Carolina, Chapel Hill.

Vice-President—Charles E. Brewer, Wake Forest, N. C.

Secretary and Treasurer—W. A. Withers, Raleigh, N. C.

The following papers were read :

" Absorptive Power of the Soil for Bases and Its Relation to Fertility," by Prof. Withers.

" A Study of the Zirconates," by Dr. Venable and Mr. Clark.

" Notes on the Reduction of Methylenedi-*o-p-m*-nitraniline," by Dr. Baskerville.

NEW YORK SECTION.

The regular meeting of the New York Section was held at the College of the City of New York, on Friday evening, March 6th, at 8:30 o'clock, Professor P. T. Austen in the chair.

The following papers were read :

" The Cassel-Hinman Gold and Bromine Process," by P. C. McIlhiney."

" The Specific Gravity of Glue Solutions," by E. R. Hewitt.

" Investigations in the Chemistry of Nutrition," by Dr. W. O. Atwater.

Mr. McIlhiney enumerated the advantages of bromine over chlorine in the gold extraction process as (1) greater solubility of bromine, as three and two-tenths per cent. against 0.76 per cent.; (2) lesser oxidizing power, whereby the iron pyrites is less acted upon; (3) greater solvent power for gold.

The bromine is recovered by distillation with live steam in stone tanks, after addition of sulphuric acid and an oxidizing agent.

The process is especially adapted to low grade telluride ores, which have not hitherto been profitably worked.

Mr. Cassel, being present, was asked to what extent the process had been worked, and whether ores containing sulphides could be treated. He replied that fifty tons *per diem* had been treated since January 1st, and the capacity was to be increased; that ores containing small amounts of sulphides had been successfully treated, using very weak solution of bromine, and eighty per cent. of the bromine had been recovered; but it was best to roast sulphide ores. The cost, including roasting, was $1.75 per ton.

Mr. Hewitt, in his work on the " Specific Gravity of Glue Solutions," had obtained his results from experiments on all grades of glue from the best photographic gelatine, to the darkest and poorest grades in the market.

He found the expansion of glue solutions to be the same as water alone; that the specific gravity of glue containing water was less than in the dry state; that the hydrometer could not be used in solutions containing over sixty-five per cent., and that the quality of the glue had no effect on the specific gravity of the solutions.

He concludes that there is a series of distinct chemical combinations of glue with water.

In the discussion of the paper, Dr. Horne asked if the specific-gravity of a glue solution could be determined by dropping it into some solution of known density, not acting on the glue solution.

Mr. Hewitt replied that this method had been tried, using xylol, chloroform, and some other liquids, but the results were not as satisfactory as could be obtained by the hydrometer.

The presence of Dr. C. B. Dudley, president of the society, was then announced, and Dr. Dudley addressed the meeting in part as follows:

"*Gentlemen of the New York Section:* It has been a rare pleasure to attend this meeting of the New York Section, and I would like to congratulate you on one or two points. First, the advantage that comes to you from being able to meet together, read papers, shake hands, and dine together. I am so far away from the chemists that it does me good to meet and shake hands with a chemist. In the early days of the Pittsburg Society I tried to meet with them and have been present on many enjoyable occasions, but having joined the society when there was only a New York Section, I have felt at home with you and have wished I could meet with you oftener.

"Another thing on which I wish to congratulate you. Our General Secretary informs me that we have a good round thousand now in our membership. There are those of you who have stood by the society when it was not as prosperous as it is now, who can appreciate this.

"Now as to what is to be done in the field of our labors. My daily work, or a great part of it, is with iron and steel, and if I could, I would give all my time to the study of pig iron.

"There are many problems yet to be solved in regard to it,

and of which a great deal might be said, but as there are other papers to come before you this evening, I will not detain you longer. I am very glad to have been able to meet with you."

Dr. W. O. Atwater was then introduced, and after giving a synopsis of the work which had been done in other countries, especially in Germany, on the chemistry of food and nutrition, he described the progress which had been made in this country, beginning with the early work of Professor Baird, then of the Smithsonian Institute, who gave the first impulse to this work by his studies of the food value of a number of varieties of fish. He then passed to a description of the work recently done under his direction and that now in progress in determining the heats of combustion, or fuel values of food. He said that we know the laws of conservation of energy hold good in the living organism, but we do not yet know *how* they hold good. We must study these things in the living organism, and for this paper a respiratory calorimeter has been constructed at Middletown by which the experimental determination of heat of radiation, energy of food consumed, etc., is to be obtained. A man had been kept in this apparatus for four days, and it was expected to arrange to extend the experiment to a week or even several weeks.

Eight attendants were required to run these experiments.

Dr. Dudley asked whether Professor Atwater had used a current of oxygen instead of potassium chlorate in his experiments on the heats of combustion of foods, and stated that he had used the oxygen with very satisfactory results in determinations of calorific value of coal.

Dr. Dudley also asked whether the quality of the fat of animals was dependent on the food.

Professor Atwater replied that the fat formation is a function of both the organism and the food.

On motion of the secretary, a vote of thanks was passed to Professor Atwater for his interesting report on the progress of the chemistry of nutrition.

Professor Breneman moved that a committee be appointed to make a report at the next meeting on the feasibility of organizing a chemical club from the members of the New York Section. Seconded and carried.

The Chair appointed Messrs. Breneman, McMurtrie, and Hallock.

The Librarian announced the receipt of a bequest from Dr. A. A. Fesquet, of two microscopes and accessories. The Chair directed that a suitable recognition of the gift be made.

RHODE ISLAND SECTION.

The regular meeting of the Rhode Island Section was held at Providence, Thursday evening, Feb. 13, 1896. Mr. Chas. S. Bush in the chair.

A paper was read by Mr. Charles E. Swett. Subject, "Ultramarine."

The reader presented the results of a few experiments he had performed upon ultramarine, with some of the more common reagents.

The March meeting was held on the 19th inst., at Providence. Chairman C. A. Catlin, presiding.

Mr. Walter E. Smith read a paper upon "The Origin of Petroleum."

In brief, the paper was as follows:

The theories given for the origin of petroleum are in general divided into three classes:

1. The chemical theories advanced by Berthelot and Mendeléeff, that water on metallic carbides forms acetylene, which is further changed.

2. The theory that it is indigenous to the rocks in which it is found.

3. The theory that it is a distillate formed from highly organized substances.

VOL. XVIII. [APRIL, 1896.] NO. 4.

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THE MANUFACTURE OF CALCIUM CARBIDE.[1]

BY J. T. MOREHEAD AND G. DE CHALMOT.

Received January 27, 1895.

SO universal is the interest in acetylene gas and so different the estimates and opinions as to the cost of calcium carbide as a source of the cheap production of acetylene gas, that we have thought it desirable to place on record the data from our actual experience in the production of calcium carbide in quantities. The works of the Willson Aluminum Company have been running night and day since May 1st, 1895, producing calcium carbide. These works are daily duplicating the results here given and can expand indefinitely. Each individual step, except water power, as taken at Spray, N. C., is capable of being changed in the direction of reducing the cost of the output, as these efforts have been attended with the clumsiness, lack of adaptability and excessive cost that is incident to all efforts along an untrodden path. Still we can produce calcium carbide at less than $25.00 per ton, including wear and tear and interest on capital.

Beyond looking after the dynamos, no special training is necessary, as neither metallurgical nor chemical skill is required in the operations. We grind and mix coke and lime, start the water wheel, see that the arc is formed, shovel in the mixture of lime and coke and the volt- and ammeter show when to lower or

[1] Read Sept. 3d, before the Springfield meeting of the A. A. A. S. by one of us (M). We have made since then several additions, so as to make the article complete up to the present time.

raise the carbon pencils, which is done by means of a screw located in the dynamo room, away from the furnace. We can measure with an ordinary yard stick on this screw the height of the piece of carbide in the furnace. We stop when we have raised the carbon pencils thirty-three inches, switch the current off to another furnace and repeat the operation. The carbide in the former furnace, as soon as cooled and brought in contact with water, is all ready to do perfect work in generating acetylene gas; it will proceed with this work without help and will make room therefor in spite even of bands of steel.

Water power costs us $6.00 per horse power. Water in the raceways ready for the water wheels is now offered in enormous quantities to the Willson Aluminum Company at the rate of $5.00 per horse power per year. These powers are located at different places, where coke and lime can be had cheaply, and also cheap transportation for the carbide to the market.

The technical description of our process which follows herewith was written by G. de Chalmot, who has had for some time personal supervision of the operations of the Willson Aluminum Company.

In the year 1888 Mr. T. L. Willson started a series of experiments with a view of reducing refractory ores in the electric furnace, and among other valuable things he made calcium carbide.[1]

We will first give a short description of the furnace and a general outline of the process, then enlarge somewhat on the details. The furnace used in Spray, N. C., is built of ordinary brick (a sectional front view is given in figure 1). The front side is formed by four iron doors, the one above the other. The upper two remain closed usually. The chimney is attached near the top of the furnace, and commences with a flue m in the corner. The furnace measures at the bottom inside two and one-half by three feet. The electric current enters at the bottom

[1] We will note here that Moissan, who discovered this process for making carbide, independently of Mr. Willson, communicated incidentally at the meeting of the French Academy of December 12th, 1892, (*Compt. Rend.*, 115, 1033) that a carbide of calcium is formed if calcium oxide is heated in an electric furnace with carbon electrodes. He investigated the compound much later (*Compt. Rend.*, 118, 50). Mr. Willson, who sent during the summer of 1892 samples of carbide for examination to Lord Kelvin, of the Glasgow University, clearly antedates Moissan. See Journal of Franklin Institute of 1895, page 333.—Note.

and top. The bottom electrode is an iron plate a covered with eight inches of carbon b. For this covering we use pieces of

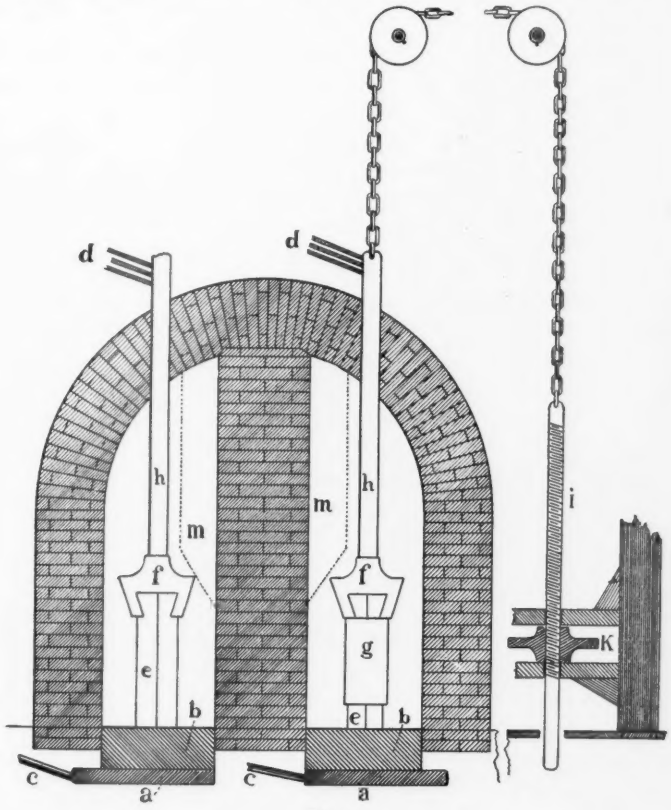

Fig. 1.

carbon pencils or a mixture of coke and coal tar. Sixteen copper cables of 0.75 inch in diameter c convey the electricity from the dynamos to the bottom electrode.

Sixteen other cables are connected with the top electrode d. The top electrode is composed of six carbon pencils e, each four inches square and thirty-six inches long. Six pencils are

arranged in three pairs behind each other and are cut out at the top so as to fit in the carbon holder f. They are enveloped together by a sheet of iron g, which is shown in the right-handed furnace of figure 1. They really form one pencil. The carbon holder is screwed to a copper bar h, which is three inches square and to which the copper cables are connected. This bar is fastened by a chain that runs over two pulleys to a long upright screw i. On this screw is a nut which forms the center of a wheel k. By turning the wheel the screw can be raised or lowered. The man who attends to the wheel has the volt- and ammeter before him. The electric current is generated in two dynamos to which transformers are connected, and which can give a current of from fifty to 100 volts. The power is furnished by a water wheel of 300 horse power under twenty-eight feet fall.

Two of the furnaces have been working for twelve months and they have given satisfaction, except for working not sufficiently economically. In the furnaces built for the Niagara Falls Carbide plant, many changes which we suggested, have been adopted, looking to economy of production. We give here a short description of these furnaces (figures 2 and 3).

In Spray it is necessary to allow the furnace to cool before emptying it. In order to use one and the same furnace continuously, the bottom of the furnace is replaced by an iron car a which runs on a track and in which carbide is formed. When the car is filled the pencils b have been lifted entirely out of it. The current is then shut off, door c is opened, the full car is run out and replaced by an empty car. The pencils are lowered again to the bottom of the car and a new run is commenced.

The bottom of the car is covered with from four to eight inches of carbon. When the contents of the car have sufficiently cooled outside the furnace, which will take from six to twelve hours, the body of the car is lifted from the track by the trunnions d and turned over. The contents are dropped on a grate formed of iron bars, on which the piece of carbide remains, while the unreduced material falls through into a lower room where it is collected to be used again for the formation of carbide. The mixture of lime and coke is fed into the car through the flues e,

which extend along the whole length of the car. The rods f which bear four blades, extend through the whole breadth of

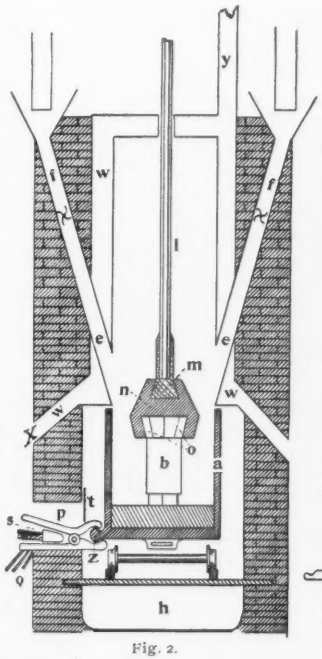

Fig. 2.

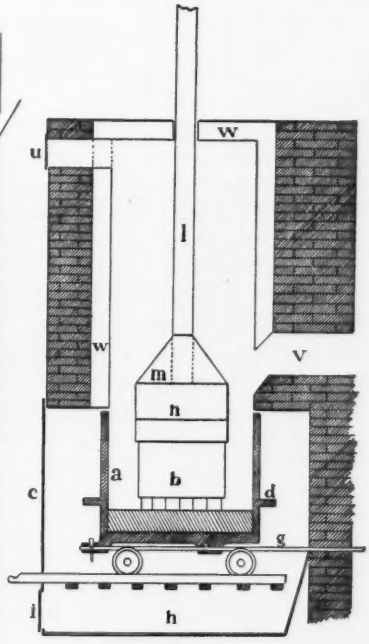

Fig. 3.

the feeding flues. These rods are turned automatically, and the faster they turn, the more material is fed into the car. In order to stoke the furnace automatically, the car is attached to an iron bar g by two hangers and a coupling in front of the car. Bar g extends through the back wall of the furnace, and is automatically moved forward and backward for about two inches and about twenty times per minute. The car is thus also rolled backward and forward on the track for about two inches each time. Every time that the car stops or starts it gets a little jerk which is sufficient to fill up the holes made by the escaping gases in the loose material. This motion of the car further prevents the arc being located for a longer time at one point, for

which the arc has always a great tendency. This will materially increase the efficient use of the heat of the arc. Under the track of the car is the bin h in which the unreduced material is collected that will fall from the car when this is taken out. This material can from time to time be taken out through the door i. The carbon holder is more complicated than in the Spray furnace. Twelve carbons are used and the holder is therefore about twice as heavy. It is not advisable to suspend this carbon holder from a copper bar, which moreover becomes rather hot in this closed furnace. The carbon holder is therefore attached to a rod l, which is composed of three slabs. The inner one is of copper and measures six by one and one-half inches, and the outer ones are of iron and are six inches by one. Since it is not practical to attach the twelve carbons in their iron casings to the carbon holder in the furnace, the holder itself is composed of two pieces, m and n, which slide into each other. The aggregate of pencils is connected to piece n outside the furnace and the whole is placed in the car a. Rod l is so far lowered that piece m will easily slide into piece n, and the connection can easily be effected. Iron plates o are placed between the carbon holder proper and the pencils. These plates o are about one inch thick. They are fastened to the inside of the carbon holder by pins which are inserted in the holder, and fit in holes of the plates. These plates can be easily removed and replaced. It will sometimes happen that a small arc is started between the pencils and the inside of the carbon holder and a part of the carbon holder will melt. In the case that the plates o are used, one can simply replace these plates. The car a forms one of the electrodes and is connected with the bottom cables q by two clamps p. The lower clamp is stationary and the upper one can be opened. The clamps are tightened around the appendage z of the car by a wedge and screw s. When the clamps are fastened the slide t is lowered so as to shut the opening. The electric connection with the car can also be and is better made through the bar g, which in that case is composed of an iron and copper slab. It may also be made by two copper bars which run alongside of the car and are pressed against it with springs. The furnace is entirely closed.

When it is started the door c is shut, but the door u is kept open till the carbon monoxide, which is formed in the reaction, has replaced the air in the furnace. This point is reached when the flame comes out of this door. Door u is then also closed and the gases escape through the chimney v. The use of door u prevents explosions of the carbon monoxide in the closed furnace. Chimney v begins just over the car. The carbon holder and the rod l are therefore not in the current of the hot gases. The upper part of the furnace is cooled moreover by an air jacket w through which a draught of air is maintained. The cold air enters through openings x and the warm air is led off by chimney y. The warm air may be utilized for heating the building. The chimney gases pass through flues or rooms, in which the lime dust is collected by proper means. Owing to valuable suggestions of our superintendent, Mr. J. C. King, this furnace is called the King furnace. Besides these two types of furnaces, several others have been proposed.

In order to start our present furnace, we shut the lower iron door and lower the pencils to the bottom of the furnace. The current is turned on and the mixture of coke and lime fed in, the arc being kept covered with the mixture as high as one foot around the pencils. It is then easier to keep the arc steady. It is necessary to stoke from time to time, for the gases which are formed in the arc constantly make channels through the material, and especially if unslacked lime is used. These channels will not fall in and less material will come into the arc. The feeding in of the material is continued for several hours. If the attendant at the hand wheel sees that the voltage becomes low, he raises the pencils. If the arc should be broken the amperage becomes zero and the voltage high, and in that case the pencils are quickly lowered. After shutting off the current it is well to allow the furnace to cool two or three hours before emptying it.

The carbide is always found in one piece between the pencils and the bottom. It has a conical form, being broader at the base and can be two and one-half feet high in our furnace. It however never has so great a diameter as to fill up the whole capacity of the furnace. The carbide is therefore entirely sur-

rounded by a cover of the mixture of lime and coke. This mixture is so bad a conductor of heat that the brick walls of the furnace are not attacked. It is very easy to separate the carbide from the loose mixture, for the latter never melts, together, while the carbide is hard and solid. The pieces of carbide are covered with a thin coating which is a little thicker at the top of the piece, and the same may be reground and again used. This coating contains mainly carbon, but also carbide and calcium oxide. It seldom yields more than a half cubic foot of gas per pound, but in some cases it yields 1.77 and even 2.10 cubic feet. This coating, however, is of little importance. If the mixture is well made this coating seldom exceeds from twenty to thirty pounds on a piece of carbide of from 300 to 400 pounds. The carbide itself is crystalline. The crystals are especially well developed near the top and are more perfect with an excess of coke, low voltage and when allowed to cool slowly. The center of the piece of carbide stays liquid for some time after the electric current has been shut off. The liquid part, however, is of the same quality as the rest of the piece. We have in fact tapped out of the furnace, carbide which was very pure and yielded 5.59 cubic feet of gas per pound. We do not wish to express an opinion as to the practicability of tapping the carbide as soon as it is formed. We will only mention that Mr. Price, in Newark, has, with a view of tapping the carbide, constructed and patented a new furnace, and that one of us (C.) has also devised a furnace for the same purpose.

Carbide of average quality (about five cubic feet of gas per pound) often has a reddish color, especially if it has been made with a current of high voltage. Carbide of bad quality is often grayish or blackish, or will show streaks of graphite. Pure carbide yields more than 5.90 cubic feet of gas per pound. It has, however, been found to be more economical to produce carbide that yields only about five cubic feet of gas per pound. Samples of carbide of different qualities contained:

TABLE I.

Cubic feet gas per pound.	Carbide. Per cent.	Free calcium oxide. Per cent.	Carbon. Per cent.	Other impurities. Per cent.
5.7	96.6	0.6	....	2.8
5.5	93.2	4.2	....	2.6
5.1	86.4	9.5	....	4.1
5.025	84.7	10.7	1.6	3.0
3.6	61.0	27.5	3.2	8.3
3.45	58.5	1.1	25.6	14.8

The upper part of a piece of carbide is often purer than the under part.

The coke to be used should not contain much ash. Our coke contains about seven per cent. of ash. The carbide obtained with a coke of from ten to eleven per cent. of ash was perceptibly inferior to that obtained with our usual coke. It was found impracticable to make a good quality of carbide with a coke of twenty-seven per cent. ash. It is well that there should not be more than ten per cent. of ash in the coke. The coke should be ground very fine, and it should pass through a fifty mesh sieve. The lime need not be as fine as the coke. The largest pieces should pass through a ten mesh sieve. If the lime is coarser the quality of the carbide becomes inferior. That the state of the pulverization of the lime is important, can be seen by a comparison of the average amount of gas per pound (4.97 cubic feet), obtained with unslaked lime (Table II), and that obtained with air-slaked lime (5.27 cubic feet Table III). The unslaked lime was in several instances not quite as fine as the slaked lime. Unslaked lime is decidedly preferable to air-slaked lime, as we will see afterwards.

The lime which we use contains one and one-half per cent. magnesia and one per cent. of the other impurities. The anhydrous lime should contain ninety-five per cent. calcium oxide, and no more than five per cent. impurities. The presence of magnesia is especially detrimental to the production of carbide. We could not obtain a good quality of carbide with a lime in the following analysis: Insoluble, 0.24 per cent.; silica, 0.78 per cent.; ferric oxide and alumina, 0.68 per cent.; calcium oxide, 92.83 per cent.; magnesium oxide, 5.47 per cent. Further experiments showed that two and one-half per cent. of magnesia in

the mixture has a marked influence on the production. The lime used for making carbide should not contain over three per cent. of magnesia. That magnesia has such a bad influence upon the formation of carbide is probably due to its forming a veil between the carbon and the lime particles preventing their combination. Magnesia does not unite either with lime or with carbon. The latter fact was first shown by Moissan,[1] and our own experiments in this line fully confirm his results. The lime and the coke must be mixed very well or the carbide will be of inferior quality and there will be much coating. Besides the carbide some mixture remains in the furnace. More carbon than lime burns out or volatilizes in an open furnace. It is therefore necessary to add carbon to this mixture before using it again. The amount to be added is calculated from the result of an analysis of the mixture. If coke is added in the proper proportions, the unsmelted portion of the material can be returned at least three times into the furnace, and still yield good carbide. The impurities of the lime and the coke ashes remain as well in the carbide as in the residual mixture. It is therefore a good practice to add charcoal instead of coke to the mixture, so as not perceptibly to increase the amount of ash. The mixture that comes from the furnace is red hot and it will stay hot for days. It will lose a large amount of carbon if allowed to lay in heaps in the air. It is better to mix in the necessary amounts of carbon and use the mixture at once again. One can also keep the mixture in air-tight sheet-iron tanks. If the lime has been unslaked the mixture cools much quicker and does not lose as much carbon after it has been taken from the furnace. In the case of slaked lime, water gas is probably formed in large amounts. The carbon pencils must be well cared for in order that they last for a long time. If sufficient coke is put in the mixture they are not attacked much at the end. They will shorten from 0.05 to 0.10 inch for every hour running. They become thinner for being exposed to the air when hot. They are mainly attacked after the electric current has been shut off, for if the furnace is working the gases from the arc come up around the carbons and shut the air off. In order to save the

[1] *Compt. rend.*, 118, 506.

carbons best it is therefore well to keep the furnaces running with as little interruption as possible. In the closed furnace, which we have described, the carbons will be surrounded by non-oxidizing gases, which will save them materially. In the open furnaces in Spray we surround the carbons with a sheet iron cover that reaches from the carbon holder to within four inches of the bottom end of the carbons. This jacket is fastened with iron wires to the carbon holder. The space between the carbons and the jacket is packed with a mixture of coke and coal tar or pitch. This mixture is baked by surrounding the carbons and jacket with the red hot material that comes from the furnace or by placing them in a fire. The jacket will generally last as long as the carbons. One set of the carbons in an open furnace and with interrupted operations will last on an average about 100 hours. These figures hold good where a current of from 1,700 to 2,000 amperes is used. The voltage has no perceptible influence on the result. Working with say 1,700 amperes and 100 volts and generating about 225 horse power, the production of carbide per hour can be reckoned to be easily eighty-five pounds, and one set of carbons can therefore make at least 8,500 pounds of carbide, even in an open furnace. If the furnace is used continuously the carbons will last at least from 200 to 300 hours, and the cost of pencils for one ton of carbide will be about $1.00.

The analytical part of our work has been very simple. After the piece of carbide has been broken open with a hammer, two or more samples, representing as nearly as possible the average quality of the carbide and of about eight ounces each, are taken. These samples are broken in pieces of about one-half inch in diameter and from two to three ounces are taken for one gas test. The material is put into a dry bottle of about one quart capacity, which is provided with a rubber stopper, through which two glass tubes pass. The one tube bears a stop-cock and drop funnel, the other tube conducts the gas through a series of U-tubes and then through a small gas-meter. The funnel is filled with water, and by opening the stop-cock, water is allowed to drop slowly on the carbide. The acetylene gas is generated and is cooled in the U-tubes before it passes to the

gas-meter. Much water vapor is condensed in the U-tubes, for the gases generated in the bottle are hot. We make a correction for the temperature of the gas as it passes the gas-meter. We do not take into consideration the small amount of gas which passes through the gas-meter by the expansion of the gas in the bottle when the latter becomes hot, and because a part of the bottle becomes filled with water. The error arising herefrom is of no consequence, for the volume of the bottle is only one quart and the volume of the gas which passes from the gas-meter is from one-half to one cubic foot. The water, moreover, becomes saturated with acetylene. Our figures show the amount of moist gas at the temperatures of 60° F.

In order to determine the lime in the mixture, two and five-tenths grams are boiled with a slight excess of hydrochloric acid of known strength in a 250 cc. bottle. The bottle is cooled and filled up. The liquid is filtered and in fifty cc. of the filtrate the excess of acid is determined by titration. The coke is determined by boiling two grams of mixture with twenty-five cc. of twelve per cent. hydrochloric acid and filtering off the coke on a Gooch crucible. These methods do not make a claim to absolute accuracy, but they can be quickly executed and give a good estimate of the relation in which the coke and lime are present in the mixture, as the following figures show. The coke used for the original mixture contained 7.33 per cent. of ash. The coke that remained from the mixture that had been boiled with twelve per cent. hydrochloric acid contained six and eight-tenths per cent. of ash, and the coke which remained by the same treatment from a similar mixture that had been once in the furnace contained seven and eight-tenths per cent. ash. The amount of lime found in mixtures by titration and that found by gravimetric analysis varied only by from one-half to three-quarters per cent. when the small amount of magnesia in the lime was known and taken into consideration. In controlling the different runs we have proceeded as follows:

The carbide was weighed and the coating on it determined either by takng it off and weighing it or by estimating it on small and clean pieces. By deducting the weight of the coating from the weight of the piece of carbide we obtain the net yield

of carbide. The gas therein is determined, the figure accepted being the average of the result of the analyses of at least two samples. In order to determine the power used, we multiply the voltage by the amperage and divide the product by 746 to obtain the number of horse power generated by the dynamos. In order to make a more proper comparison we found it necessary to deduct the loss of voltage sustained in the carbon pencils. Our pencils were made in different factories and had a different resistance. We therefore determined the difference in voltage as indicated by the usual reading of our meter and the voltage at the end of the carbon pencils. We touch the end of each pencil alternately with an iron rod that is connected with the volt-meter by a copper wire. We call net power the power generated by the dynamos less the average loss in the six carbon pencils. Our meters are placed in the primary circuit and we have not taken into account the losses of amperage in the transformers and those sustained by leakage. We have further found that the readings of our meters are about six per cent. higher than those of standard Weston meters. It may therefore be safely relied upon that all our estimates for the production of carbide per horse power are too low. The error is, however, in all cases in the same direction, so that it cannot have materially influenced our deductions, which are based upon a comparison of our results.

In the carbide there is also a considerable loss of voltage and therefore of power. We found, for example, sixty-five volts in the bottom cables and only fifty volts at the top of a two and a half feet high piece of carbide just under the arc. This makes a loss of six volts for each one foot of carbide. The average production during six to eight hours of continuous working is as large as that during two or three hours at the same power. It is, however, not advisable to make the carbide pieces higher than two and a half feet, since then the resistance of the carbide will begin to materially reduce the quantity of the production.

Taking into account the weight of the product, the time in which it has been produced and the number of horse power used, we calculate for each run the amount of pounds produced per horse

power in twenty-four hours. By multiplying these figures by the number of cubic feet of gas produced per pound we obtained the number of cubic feet of gas produced per horse power in twenty-four hours. In the following table we give the results of experiments wherein everything has been determined, wherein both unslaked and slaked lime have been used and voltage, amperage, and duration of runs were varied. Since these results were obtained we have had many visitors from all parts of the country and for each party we have made a test run. The results of these runs have all confirmed our previous results, with one exception, which was due to the presence of five and a half per cent. magnesia in the lime.

TABLE II. UNSLAKED LIME.

Date.	Time of experiment.	Volts.	Amperes.	Loss of voltage in the pencils.	Horse power.	Production in twenty-four hours including slag.	Net production.	Cubic feet of gas per hour.	Cubic feet of gas per horse power in twenty-four hours.
	Hours.			Per cent.		Pounds.	Pounds.		
June 27th	2.50	100	1700	7.0	214	9.87	9.42	4.83	45.50
July 2nd	3.00	100	1666	8.0	205	10.34	9.76	5.25	51.24
" 1st	2.25	100	1700	10.0	205	10.66	10.10	4.66	47.06
June 24th	3.20	100	1600	7.0	214	11.50	10.73	4.93	52.90
" 28th	2.50	100	1700	10.0	205	11.70	11.10	4.75	52.72
July 18th	3.00	65	2000	5.0	165	9.63	9.15	4.95	45.29
" 19th	3.00	65	1900	5.0	158	10.40	9.62	4.83	46.46
" 5th	3.75	65	2000	5.0	165	8.38	8.15	5.40	44.01
" 9th	4.50	65	2000	5.0	165	9.50	9.05	4.99	45.16
Aug. 10th	6.00	65	1800	8.0	144	9.34	9.00	5.39	48.51
" 13th	6.00	65	1800	8.0	144	10.83	10.44	4.82	50.32
July 31st	7.00	75	1800	8.5	166	11.44	10.53	4.83	50.86
					Average,		9.75	4.97	48.33

TABLE III. AIR-SLAKED LIME.

Date.	Time of experiment.	Volts.	Amperes.	Loss of voltage in the pencils.	Horse power.	Production per horse power in twenty-four hours, including slag.	Net production.	Cubic feet of gas per pound.	Cubic feet of gas per horse power in twenty-four hours.
	Hours			Per cent.		Pounds.	Pounds.		
June 25th	5.00	100	1700	7.0	214	8.34	7.96	5.30	42.19
" 29th	4.00	100	1700	10.0	205	8.78	8.34	4.98	41.53
" 19th	5.50	100	1700	7.0	214	9.25	....	4.89	....
" 22nd	4.00	100	1600	7.0	199	9.80	9.65	4.74	45.75
Aug. 14th	4.50	75	1700	7.0	159	7.88	7.13	5.50	39.22
July 12th	3.75	85	1800	3.5	198	...	6.33	5.55	35.13
" 26th	8.00	75	1800	5.0	172	8.40	7.23	5.33	38.54
" 12th	5.50	85	1775	8.0	185	...	7.32	5.32	38.94
" 6th	5.00	80	1020	3.0	200	8.78	8.16	5.11	41.70
" 23rd	3.00	65	1800	5.0	150	6.83	6.40	5.78	56.99
" 22nd	2.00	65	1800	5.0	150	7.13	6.40	5.62	35.97
" 22nd	2.00	65	1800	5.0	150	7.20	6.40	5.64	36.09
" 25th	9.00	65	1800	5.0	150	7.72	7.27	5.54	40.28
" 20th	4.00	65	1800	5.0	150	8.60	8.00	5.01	40.08
" 23rd	5.00	65	1800	5.0	150	9.02	8.00	5.07	40.56
" 24th	8.00	65	1800	5.0	150	9.30	8.03	4.97	39.91
					Average,		7.51	5.27	39.52

It is obvious that the results obtained from unslaked lime are far better than those with air-slaked lime. This is undoubtedly due to a loss of power used in decomposing the hydrated lime. The unslaked lime used by us contained, after being ground, from five to nine per cent. of water. In practice it is necessary to use the mixture that comes from the furnace again. This mixture always contains some carbonate of lime, but if it be mixed when still hot with the necessary amount of carbon and put again into the furnace the lime has no opportunity to slake. The unslaked lime has the further advantage that it weighs less and is much less bulky, and that the mixtures made from it cool much faster than those made from slaked lime. The only disadvantages of unslacked lime are, that it must be ground and that mixtures made from it require more stoking if put into the furnace. The mixtures of unslaked lime can stand up against the sides of the furnace under a very steep incline and they can leave a hole all around the pencils. The mixture to be used should, on an average, contain 100 parts of

lime and sixty-four to sixty-five parts of carbon in order to obtain a carbide of about five cubic feet of gas per pound. If the voltage is increased to 100 it is better to take a little more carbon (100 lime and sixty-six to sixty-seven carbon). If the voltage is sixty-five or less, sixty-three to sixty-four parts of carbon are sufficient. If the amount of carbon is increased the carbide becomes purer, but there is often more coating.

The largest amount of gas per horse power is obtained if the carbide yields about five cubic feet of gas per pound. The yield of carbide in pounds varies inversely with the quality. In the following table we give the results of a series of experiments made with slaked lime and with a current of sixty-five volts and from 1,700 to 2,000 amperes. Several of these experiments have not been taken up in Table II, because the amount of slag on all the pieces of carbide has not been determined.

Date.	Production per horse power including slag. Pounds.	Cubic feet gas per pound.
July 23rd	6.85	5.78
June 14th	7.10	5.80
July 22nd	7.13	5.62
" 22nd	7.20	5.64
" 25th	7.72	5.54
Aug. 14th	7.88	5.50
May 21st	8.10	5.20
" 22nd	8.30	5.10
July 26th	8.40	5.33
June 4th	8.46	5.52
July 20th	8.60	5.01
June 5th	8.76	4.94
May 28th	8.80	5.20
" 23rd	8.82	5.10
July 23rd	9.02	5.07
June 8th	9.06	5.10
" 24th	9.30	4.97
July 11th	9.30	4.33
Aug. 12th	9.44	4.51
May 31st	9.87	4.30
Aug. 8th	10.52	4.23

Carbide has been made successfully in Spray by the use of both the direct and the alternating current. We cannot express

an opinion as to what current can be used to the best advantage, for we are not able to compare results. All the results communicated in this paper have been obtained by the use of the alternating current. That electrolysis plays a part in the carbide manufacturing process of Mr. Willson is therefore out of the question, and we do not need to use a furnace of the Moissan construction to prove this. It is not desirable to increase the amperage over 2,000 if only six carbons of four inches square are used. The higher the amperage the greater the loss of voltage in the pencils and therewith that of power. The carbons will also last longer if the amperage is low, because they do not become so hot. Lastly we did not obtain as great a yield per horse power if the amperage was high and the voltage correspondingly low. We obtained the best yield of gas per horse power by using a current of 100 volts, which can be seen by comparing the average of the results in Table II.

TABLE V.

	Volts.	Horse power.	No. of experiment.	Average cubic feet of gas per horse power in twenty-four hours.
Unslaked lime ..	100	205–214	5	49.88
	65–75	144–165	7	47.23
Slaked lime.....	100	200–214	3	43.15
	75–85	159–100	5	38.71
	65	150	7	38.55

It must be taken into account that we measured the primary current and that the losses of amperage in the transformers probably have been higher when we did not use the highest voltage, *i. e.*, 100. We do not know in how far it would be advisable to increase the voltage over 100, since our dynamos cannot give us a current of more than 100 volts. We believe, however, that the heaty ielded by an arc of 100 volts and from 1,700 to 2,000 amperes is about the largest amount to be profitably used for the production of carbide in one furnace with six pencils, as it is used in Spray. We base our assumption on the following facts: The quality of the carbide becomes better if the voltage decreases. We experienced some trouble in obtaining large carbide crystals with an arc of 100 volts and 1,700 amperes, and in order to obtain a carbide that yields more than five cubic

feet of gas per pound the mixture should contain an excess of carbon. If a current of 100 volts and 1,700 amperes is used the furnace requires more attendance and stoking than if a lower power and especially a lower voltage is used. The higher the voltage the faster the pencils must be raised, for if the voltage is low (fifty or sixty-five) the carbide spreads out much more than if the voltage is high (100 volts). In the latter case the carbide builds up as a long thin piece and it is oftener necessary to empty the furnace. As to the time that one furnace should be used continuously, we wish to say that we did not perceive a difference in the quantity and quality of the product whether we ran three hours or from three to nine hours. We must, however, remark that in the case where we used 100 volts and 1,700 amperes with mixtures of unslacked lime we could not continue running for much more than three hours because the construction of the furnace did not admit of raising the pencils quite three feet. With slaked lime we made also with this high power very satisfactory runs of five and five and a half hours. During the first hour the production is somewhat lower. It seems that more heat is lost probably for heating up the furnace.

The mixture used in all of the following experiments contained lime, 50.08 per cent., and coke,[1] 39.22 per cent. The current was of sixty-five volts and 1,800 amperes, the loss of voltage in the pencils five per cent. and the net horse power 150.

TABLE VI.

Time of experiment. hours.	Production per hour in pounds.	Cubic feet of gas per pound.	Cubic feet of gas per hour.
1	37	5.63	208.31
2	40	5.62	224.80
2	40	5.64	225.60
3	40	5.78	237.20

We have now still to consider a very important question, namely, how much coke and lime are necessary to produce one pound of carbide. The formation of carbide taking place according to the following formula:

$$\underset{56}{CaO} + \underset{36}{3C} = \underset{28}{CO} + \underset{64}{CaC_2}$$

0.563 pound of carbon and 0.875 pound of calcium oxide are

[1] Of 92.17 per cent. of carbon.

theoretical necessary to yield one pound of carbide. The carbide of five cubic feet of gas per pound contains, however, free calcium oxide. We therefore might expect that more calcium oxide and less carbon are used. In practice, however, some calcium oxide and carbon are volatilized or burned. For a succession of experiments we have weighed the mixture that was put into the furnace and that which was taken out and analyzed both. We have experienced considerable trouble in weighing the red hot material accurately and in obtaining fair samples. We have therefore not been able to observe as to how far the consumption of calcium oxide and of carbon is influenced by the circumstances that alter the quantity and quality of the product. We found, however, that less mixture is used if properly stoked and if the arc is kept covered. We found also that the losses of carbon are always more considerable than those of calcium oxide.

TABLE VII.

Number of experiment.	Amount of CaO put into the furnace.	Amount of C put into the furnace.	CaO obtained from the furnace.	C obtained from the furnace.	Amount of CaO used.	Amount of C used.	Production of clean carbide.	Amount of CaO per pound of carbide.	Amount of C used per pound of carbide.
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lb.
1	675	448	417	270	258	178	195	1.32	0.91
2	739	463	415	242	324	221	285	1.13	0.78
3	859	557	601	375	258	182	190	1.36	0.96
4	612	402	415	262	197	140	190	1.04	0.74
5	851	491	598	282	353	209	280	1.26	0.75
6	906	577	478	280	428	297	375	1.14	0.79
7	1067	699	420	238	647	461	555	1.17	0.83
8	552	375	253	167	299	208	223	1.34	0.95
9	374	211	207	115	167	96	132	1.27	0.73
10	675	461	244	134	431	327	345	1.25	0.95
							Average	1.228	0.837

TABLE VIII.

Number of experiment.	Mixture into the furnace.		Mixture out of the furnace.	
	CaO.	C.	CaO.	C.
	Per cent.	Per cent.	Per cent.	Per cent.
1	54.70	36.32	57.01	36.89
2	54.51	34.18	57.29	33.36
3	56.23	36.46	57.00	35.62
4	55.66	36.51	55.47	35.02
5	59.70	34.43	58.16	32.94
6	56.65	36.09	55.60	32.61
7	55.44	36.32	54.93	31.09
8	50.64	34.43	51.81	34.29
9	52.08	29.39	52.09	28.90
10	49.34	33.85	41.45	28.27

The average figures of table VII are rather high, for where much coke and lime have been used this is certainly partly due to losses of material by weighing into and out of the furnace and also by insufficient stoking. In the King furnace, the under part of which shuts hermetically tight and excludes draft, and which is stocked mechanically, the amount of coke and lime necessary for making one pound of carbide will certainly be much reduced. In the figures given in table VII we have left the outside coating out of the calculation. In a plant where the acetylene gas is generated at once from the carbide it would pay to use this coating also for making gas. From table VII we see that a very large percentage of the mixture is not acted on by the arc. We have, however, reduced this amount to one-third of the mixture and could reduce it still more without either injuring the furnace, the quantity and quality of the carbide, and without increasing the amount of carbon and lime necessary for making one pound of carbide. In the furnace used in Spray the inside is square instead of octagonal and the dimensions are rather too large. We therefore feed more material into the furnace than is necessary.

Besides coke we have used several other carbonaceous materials for making carbide. We have used soft coal, anthracite, charcoal, pitch, tar, rosin, and asphalt, and obtained in all cases carbide. Most of these materials are not of sufficient importance to be taken into consideration and we will only add some words about the first three.

Charcoal, owing to its small percentage of ash, yields a very pure carbide. The only drawback, besides its price, is that it is so light that the gases carry if off to a considerable amount. It is therefore necessary to add from five to ten per cent. more carbon to the mixture if charcoal is used than if coke is used.

We used a soft coal which contained volatile matter 19.84 per cent. and ash 1.48. The mixture with soft coal gave a terrific blaze. The carbide was covered with a large amount of very porous slag in which there was much graphite. The average of results of two runs are: 641 pounds per horse power in twenty-four hours and 4.33 cubic feet of gas per pound, which equals 27.75 cubic feet of gas per horse power in twenty-four hours.

We used anthracite coal, which contained volatile matter 7.95 per cent. and ash 4.02 per cent. We made two runs with slaked and two with unslaked lime. There was no appreciable difference in the use of slaked and unslaked lime. The average result of the four runs: 7.64 pounds per horse power in twenty-four hours and 4.03 cubic feet of gas per pound, which equals 30.79 cubic feet per horse power in twenty-four hours. These results are much lower than those obtained with coke. We can not therefore recommend the use of either anthracite or soft coal for making carbide. The superiority of coke and charcoal over anthracite is probably due to the porosity of the former materials, which must facilitate the volatilization of the carbon in the electric arc, which probably must precede the formation of carbide.

ON THE ACTION OF WAGNER'S REAGENT UPON CAFFEINE AND A NEW METHOD FOR THE ESTIMATION OF CAFFEINE.

By M. Gomberg.

Received February 10, 1896.

THE use of iodine in potassium iodide as a general qualitative reagent for alkaloid dates as far back as 1839.[1] It was, however, R. Wagner[2] who first employed it for the quantitative estimation of vegetable bases, and this solution has since been known as Wagner's reagent. He based his con-

1 Bouchardat: *Compt. rend.*, 9, 475.

2 *Ding. poly. J.*, 161, 40: *Ztschr. anal. Chem.*, 1, 102.

clusion upon trials with solution of quinine and cinchonine, showing that under approximately similar conditions they always require the same amount of iodine for complete precipitation. Hence empirical factors could be established which would enable one to use a standard solution of iodine for the titration of all such alkaloids as form insoluble superiodides. The method, however, was not frequently employed, for the reason that there was no experimental proof as to the constancy of composition of the precipitates. Moreover, it was noticed that some of the precipitates give up a portion of their iodine to water, *i. e.*, they are not completely insoluble. Hence concordant results could not be obtained. Later, Schweissinger[1] applied this method to the estimation of strychnin and brucine. His results have led him to the conclusion that while the method is very satisfactory for strychnine, it is far from being so for brucine. Recently Kippenberger,[2] in his research upon the isolation and separation of alkaloids for toxicological purposes, has reviewed the subject of the action of Wagner's reagent upon alkaloids, and gives considerable prominence to this as one of the best methods for the estimation of the vegetable bases. His method of procedure was practically the same as that first proposed by Wagner. The alkaloid is dissolved in acidulated water, and to the solution a tenth or twentieth normal solution of iodine in potassium iodide is gradually added until all the alkaloid is precipitated and the supernatant liquid shows a slight excess of iodine. Instead of filtering and washing the precipitate, as was done by Wagner and Schweissinger, Kippenberger allows the precipitate to settle, and either decants or filters off an aliquot portion of the mother liquid for the estimation of iodine not taken up by the alkaloid. The estimation of iodine is always done by means of a standard solution of sodium thiosulphate.

It has been usually assumed, for reasons not entirely clear, that the composition of the precipitates is $AlK.HI.I_2$, *i. e.*, diiodides of the hydriodides of the alkaloids are formed. Of the three atoms of iodine only two can be estimated directly by titration with sodium thiosulphate. The hydriodic acid is supposed to come from the potassium iodide, while the two "superio-

1 *Arch. d. Pharm.*, **64**, 615, *1885*.
2 *Ztschr. anal. Chem.*, **34**, 317; **35**, 10.

dine'' atoms are furnished by the free iodine dissolved in the potassium iodide. The quantity of an alkaloid precipitated by a known volume of Wagner's reagent is calculated on this assumption, 2I : molecular weight of alkaloid : : amount of iodine taken up : x = amount of alkaloid. Schweissinger found that the method of calculation agrees entirely with the theoretical figures for strychnine. Kippenberger has called into question the correctness of this mode of calculation. He, too, assumes that the composition of the precipitates is to be represented by the formula $AlK.HI.I_2$, but he claims that all three atoms of iodine are supplied by the free iodine, and none by the potassium iodide. Therefore the calculation of the amount of alkaloid precipitated is to be done, according to Kippenberger, by the use of the proportion, 3I : molecular weight of alkaloid : : amount of iodine taken up : x = amount of alkaloid.

The hydriodic acid, it is supposed by Kippenberger, results from the interaction of iodine and water,

$$2I + 2H_2O = 2HI + H_2O_2,$$

a reaction which is facilitated or induced by the avidity of the alkaloids to form insoluble periodides of the hydriodides. His reasons for assuming that such a peculiar reaction takes place under the simple conditions of precipitation, are too lengthy to be given here. All his arguments rest upon the assumption that all alkaloids form periodides of uniform composition, $Alk.HI.I_2$, and that the same alkaloid gives always the same periodide. Now, there is no reason, *a priori*, why this should be the case. Jörgenson's[1] extended researches show that different alkaloids, when treated under apparently the same conditions, give periodides of entirely different compositions. Thus, morphine gives with Wagner's reagent $Alk.HI.I_3$;[2] codeine furnishes with excess of Wagner's reagent $Alk.HI.I_4$; and caffeine, as will be shown, gives $Alk.HI.I_4$, etc. It is safe to say that not until we ascertain exactly the composition of the different periodides as produced under the conditions of titrations, will the use of Wagner's reagent for quantitative purposes be placed upon a sound basis.

[1] *J. prakt. Chem.*, *1870-78*, [2], **2**, 433, etc.

[2] Jörgenson, 1870 : *J. prakt. Chem.*, [2], **2**, 438.

I have dwelt at such length upon this subject, because the method for the estimation of caffeine presently to be described, is based upon experimental evidence which is entirely contradictory to Kippenberger's conclusions. Whatever the cause may be with other alkaloids, his theory as to the production of hydriodic acid from iodine and water, does not hold good in the case of caffeine.

Wagner, in describing his method, gives a list of alkaloids which are completely precipitated by iodine solution, and also mentions that "caffeine, theobromine, piperine and urea are not precipitated at all."[1] His statement, so far at least as caffeine is concerned, has stood since then uncontradicted. It has found its way not only into standard treatises and text-books,[2] but even into periodical literature of recent date. As late as 1894, Kunze,[3] in reviewing the chemistry of caffeine and theobromine, calls attention to this peculiarity of the two alkaloids. The non-precipitation of caffeine by Wagner's reagent has come to be recognized as a distinguishing feature of this alkaloid from almost all other vegetable bases.

And yet this is entirely contrary to actual facts. Instead of forming an exception, caffeine conforms to all the requirements[4] necessary in the application of this test. It is well known that most of the alkaloids as such are insoluble, or only very slightly soluble in water; they require the presence of some acid for their complete solution. In other words, alkaloids in the form of their salts, are soluble in water. Whenever Wagner's reagent is applied for the precipitation of an alkaloid, it is always applied to a solution of some salt of it, preferably acidulated with sulphuric or hydrochloric acid. Therefore, even when strictly neutral salts of alkaloids are employed, there is still the possibility of the formation of hydriodic acid, or rather of the hydriodides of the alkaloid, as for instance, $Alk.HCl + KI = Alk.HI + KCl$.

[1] *Loc. cit.*, 41.

[2] Prescott, Organic Analysis, p. 80; Allen, Comm. Organic Analysis, Vol. 3, (2). 481: Fluckiger, Reactions, (Nagelvoort's Translation), p. 26; not affected by Wagner's reagent in either neutral or acid solutions; Dragendorff, 1888. Ermittelung von Giften. says that caffein gives a dirty brown precipitate. From the text it is not improbable he used iodine in hydriodic acid.

[3] *Ztschr. anal. Chem.*, **33**, 23.

[4] This test is perhaps most frequently made in a neutral solution, representing, as customary state, free caffeine and *normal salts* of other alkaloids.

The hydriodide thus produced is at once precipitated as a periodide. Now, it so happens that caffeine is tolerably soluble in water, and it has become customary to work with solutions of caffeine as a free alkaloid, and not in the form of its salts. The question as to whether solutions of free alkaloids are precipitated with Wagner's reagent has not, to my knowledge, been studied. My preliminary experiments in that direction show that at least some alkaloids (morphine, atropine, strychnine, etc.), are precipitated. I have not examined yet whether these periodides are identical in composition with those produced from the salts of the alkaloids. But so far as caffeine is concerned, it is true that a neutral solution of it gives no precipitate when treated with a solution of iodine in potassium iodide. When however the addition of Wagner's reagent is either followed or proceeded by the addition of some dilute acid, there is at once thrown down a dark-reddish precipitate, remaining amorphous even on long standing.[1] The composition of this periodide is, as will be shown, $C_5H_{10}N_4O_2.HI.I_4$. It was obtained for analysis in many different ways—by using either caffeine or iodine in excess, and by employing different acids. The periodide produced is, however, always of the same composition. The precipitates were allowed to settle, filtered by means of a pump, washed with water to remove the excess of potassium iodide, dried on porous plates, and finally in a *vacuum* over sulphuric acid.

I. This sample was obtained by slowly adding a solution of iodine in potassium iodide to a solution of caffeine acidulated with sulphuric acid. The iodine was added until the supernatant liquid was decidedly red. The whole was allowed to stand three hours, filtered, washed and dried as described above. The total iodine was estimated in the usual way, *i. e.*, by suspending a weighed sample in water, adding sulphurous acid solution, then silver nitrate and nitric acid; filtered, washed and dried. The "exterior" iodine, *i. e.*, the iodine not as hydriodic acid,

[1] Almost the same can be said of theobromine, making allowance for the difference of solubility of the alkaloid in water. A saturated solution of it (containing one part of theobromine to 1600 of water) gives no precipitate with Wagner's reagent, but on the addition of a drop of acid there separates in a short time a crystalline periodide. Contrary to usual statements, I find that theobromine in acid solutions gives a heavy precipitate with Wagner's reagent, of a peculiar dirty-blue color.

was estimated by direct titration with standard sodium thiosulphate.

0.2002 gram gave for total iodine 0.2785 gram AgI.
..... 0.2358 " " " exterior " 0.1433 gram I.

II. This sample was obtained by adding to an acidulated solution of caffeine enough iodine to precipitate about one-half of the caffeine present.

0.2563 gram gave for total iodine 0.3591 gram AgI.
0.1659 " " " exterior " 0.0997 gram I.

III. A neutral solution of caffeine was mixed with an excess of Wagner's reagent, and to the mixture dilute sulphuric acid was gradually added so long as a precipitate was produced.

0.4039 gram gave for total iodine 0.5668 grams AgI.
0.1424 " " " exterior " 0.0866 gram I.

IV. Filtrates from I and III, on long standing, gave a deposit of dark-blue needle-like crystals, which were collected, washed and dried as before.

0.7884 gram gave for total iodine 1.1064 gram AgI.
0.4450 " " " exterior " 0.2685 gram I.

V. This was obtained by recrystallizing the amorphous precipitate from methyl alcohol.

0.2890 gram gave for exterior iodine 0.1756 gram I.

VI. Obtained by recrystallizing the amorphous periodide from hot ethyl acetate.

0.4807 gram gave for total iodine 0.6709 gram AgI.
0.2777 " " " exterior " 0.1622 gram I.

Calculated for $C_8H_{10}M_4O_2.HI.I_4$.	Per cent.	Found. I.	II.	III.	IV.	V.	VI.
Total iodine....	76.44	75.12	75.66	75.84	75.83	....	75.40
Exterior iodine.	61.15	60.79	60.11	60.81	60.34	60.76	60.22

When some of the periodide is treated with a solution of sulphur dioxide, and then extracted with chloroform, it furnishes unchanged caffeine.

The composition of this periodide of caffeine appears to be different from that described by Tilden,[1] which he obtained by exposing to sunlight an alcoholic solution of caffeine containing some hydriodic acid. The slow oxidation of the hydriodic acid

[1] *J. Chem. Soc.*, **18**, 99, *1865*.

furnished the iodine, and the compound thus obtained has the composition, according to Tilden, $2(C_8H_{10}N_4O_2HI.I_2).3H_2O$. It is a lower periodide than the one which is obtained when iodine dissolved in potassium iodide is directly added to caffeine, as the latter has the composition $C_8H_{10}N_4O_2.HI.I_4$. Tilden also mentions that by the addition of alcoholic iodine to a solution of caffeine in weak sulphuric or hydriodic acid, he obtained a deposition of black granules, which upon analysis furnished about seventy-five per cent. of total iodine. He says that it probably consists of a compound containing nine atoms of iodine. But there is hardly any doubt that he had the tetra-iodide of caffeine hydriodide.

Properties. When dry the periodide is a violet-blue amorphous powder melting at 213° C. When moist it rapidly losses iodine on exposure to air. It is permanent when dry and suffers but slight loss when heated to 100° C. Two grams heated for four hours at that temperature lost only 0.027 gram = 1.33 per cent. It losses but very little of its iodine when suspended in water, giving up enough iodine to saturate the liquid. The presence of potassium iodide in the water favors the liberation of iodine, but even then it is but slight. The periodide dissolves readily in alcohol, especially when heated, with considerable decomposition into the free base and iodine. It is more soluble in methyl alcohol and suffers less decomposition in that solvent. It can be obtained from methyl alcohol, on spontaneous evaporation of the solvent, in the form of beautiful crystals, with a metallic dark-bluish luster. When examined under the microscope the crystals appear to consist of six-sided prisms. Ether, whether cold or warm, decomposes it but slightly. The periodide is insoluble in chloroform, carbon disulphide and benzene. It is soluble without decomposition in hot ethyl acetate from which it separates on cooling as a dark granular crystalline deposit, which melts at 215° C.

Limits of Precipitation. Like most alkaloids, caffeine is precipitated by Wagner's reagent even from very dilute solutions of the base. Although not characteristic, it is yet as delicate a test for caffeine as we have. The limits of precipitation, under the influence of different acids, will appear from the following

table. The tests apply to one cc. of the solution mentioned, acidulated with two or three drops of the acid, and to this two drops of Wagner's reagent (twentieth normal) was added.

Dilution.	Sulphuric acid. Five per cent.	Hydrochloric acid. Five per cent.	nitric acid. Five per cent.	Acetic acid. Five and fifty per cent.	Oxalic acid. Five per cent.	Tartaric acid. Ten per cent.	Citric acid. Ten per cent.
1 : 250	v. heavy.	v. heavy.	v. heavy.	none.	heavy.	slight.	faint.
1 : 1000	v. heavy.	v. heavy.	v. heavy.	.....	heavy.	v. sl.	none.
1 : 1500	heavy.	heavy.	heavy.	.....	sl.	none.	.....
1 : 3000	fair.	fair.	fair.	.....	faint.	.....	.....
1 : 5000	v. sl.	sl.	sl.	.....	.....	.....	.....
1 : 8000	v. sl.	sl.	sl.	.....	.....	.....	.....
1 : 10000	none.	v. sl.	v. sl.	.....	.....	.....	.....

ESTIMATION OF CAFFEINE.

All the method for the estimation of caffeine depend upon the extraction of the alkaloid by an immiscible solvent from either a dry residue, or from its solution in water. But Spencer[1] has recently shown how difficult it is to remove the alkaloid from its solution in water. According to him, it is necessary to shake out the liquid at least seven times with chloroform, in order to remove caffeine quantitatively. It is usually stated that caffeine does not form any stable salts in a watery solution, and consequently it can be shaken out with immiscible solvents from either alkaline or acid solutions. But this is only relatively true, as will appear from the following illustrations. 1.0085 grams of caffeine were dissolved in sixty cc. of sulphuric acid (1 : 10), and this solution was repeatedly shaken out with chloroform, twenty-five cc. at a time.

10 consecutive portions of chloroform gave a total of 0.3514 gram caffeine
3 additional " " " made a " " 0.4859 " "
3 more additional portions of " " " " 0.5034 " "

The extreme delicacy of the test for caffeine by means of Wagner's reagent, has suggested the possibility of applying this reagent for the quantitative estimation of the alkaloid. Its successful application necessitates, of course, a solution of the alkaloid free from other substances that are precipitated by, or absorb iodine,—a condition requisite in the estimation of any base by

[1] *J. anal. Chem.*, **4**, 390 *1890.*

means of Wagner's reagent. This method gives very satisfactory results, as nearly theoretical as could be expected. I am indepted for the analytical data of the subjoined table to Mr. James W. Knox, holder of the Stearns' Fellowship in the School of Pharmacy. The method of procedure employed by us was practically the same as that used by Kippenberger. Definite volumes of acidulated solutions of caffeine were precipitated with a known volume of iodine in potassium iodide. After complete precipitation an aliquot portion of the supernatant liquid was obtained, either by decantation or filtration, and the excess of iodine was estimated by titrating against a tenth normal solution of sodium thiosulphate. The precipitation is best performed in a tall test-tube on foot, and the solution for titration is removed directly by immersing the end of the burette into the liquid and applying suction at the upper end. When it is desirable to filter off an aliquot portion, a filter of glass-wool and asbestos gives very satisfactory results.

We have tested the method on solutions of caffeine acidulated with sulphuric acid, the solutions being of different strengths, namely: containing 0.25 per cent. of caffeine, 0.50 per cent., 0.75 per cent., and 1.00 per cent., respectively. We have varied in different series of experiments the amounts of Wagner's reagent, employing just the theoretical quantities, a small and large excess above that, as well as the quantities below those required by the theory. Columns I, II, III, and IV give the results obtained by allowing the solutions to stand for an hour before decanting an aliquot portion for titration; column V shows the results obtained when the liquid for titration was filtered off within five minutes after the addition of Wagner's reagent. The results are calculated on the basis that the periodide has the composition $C_8H_{10}N_4O_2.HI.I_4$. The amount of alkaloid is calculated from the amount of iodine used up, by the formula,

$$4I : C_8H_{10}N_4O_2 : : 506 : 194 ;$$

i. e., one part of iodine represents 0.3834 parts of caffeine. Or, one cc. tenth normal iodine = 0.00485 grams caffeine.

The results presented below show that the estimation of caffeine by this method is very exact. The best results are obtained

	I.			II.			III.			IV.			V.		
	Solution containing 0.25 per cent. of caffeine.			Solution containing 0.50 per cent. of caffeine.			Solution containing 0.75 per cent. of caffeine.			Solution containing 1.00 per cent. of caffeine.			Solution containing 0.50 per cent. of caffeine.		
Wagner's reagent employed.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.
Theoretical quantity + 2 cc.	0.0600	0.0591 0.0589	98.33	0.1200	0.1175 0.1175	97.82	0.1500	0.1481 0.1471	98.40	0.1200	0.1182 0.1179	98.38	0.1200	0.1154 0.1165	96.78
$1\frac{1}{3}$ theoretical quantity.	0.0750	0.0749 0.0749	99.88	0.1200	0.1191 0.1189	99.17	0.1500	0.1489 0.1485	99.13	0.1200	0.1191 0.1187	99.12	0.1200	0.1196 0.1197	99.75
Twice the theoretical quantity.	0.0500	0.0502 0.0506	100.80	0.0800	0.0805 0.0789	99.63	0.1200	0.1184	98.67	0.1100	0.1091 0.1091	99.18	0.0800	0.0802 0.0791	99.63
One-half of the theoretical quantity.	0.0750	0.0363 0.0363	48.40	0.1600	0.0794 0.0794	49.62	0.2250	0.1107	49.20	0.2000	0.1067 0.1067	53.35	0.1600	0.0791 0.0791	49.44

when iodine is in considerable excess, as is evident from the figures obtained where one and one-third and twice the theoretical quantities of Wagner's reagent were used. All the results in the table were obtained on solutions of caffeine acidulated with sulphuric acid, the acidulation being tolerably strong, about one cc. of the concentrated acid to fifty cc. of the liquid. Experiments upon the influence of the acid indicate that a large excess of sulphuric acid interferes to some extent with the reaction. The amount of recovered caffeine falls as low as ninety-five per cent. of the quantity taken, when four cc. of the concentrated acid to fifty cc. of the liquid are used. The results are also not very uniform and concordant. The fact that the precipitation of caffeine by Wagner's reagent is more delicate in presence of hydrochloric acid than any other acid would make it advisable to employ that acid in quantitative estimation of the base by iodine.

This method could easily be employed for the estimation of the alkaloid in caffeine-bearing drugs. Of course, it is necessary to have the final solution of the alkaloid in water as free as possible from other substances that may be precipitated by Wagner's reagent. The estimation of caffeine by this method is likely to give higher results than have hitherto been obtained. The following procedure is recommended:[1] The drug is thoroughly digested with water for some time, by the aid of heat, cooled, and made up to a definite volume, and filtered. An aliquot portion of the filtrate is treated with lead acetate, the precipitate allowed to settle, and filtered. The whole of the filtrate, or a given portion of it, is treated with hydrogen sulphide to remove the lead, and filtered. This filtrate, after boiling off the hydrogen sulphide, is divided into two equal portions, and each treated with a definite volume of the standard iodine solution,—the first portion without the addition of any mineral acid, the second with the addition of hydrochloric or sulphuric acid. After five to ten minutes' standing the excess of iodine is estimated in each of the two solutions, as described above. The first portion, containing no other but some acetic acid, serves to indicate whether the filtrate from the lead sulphide contains any other materials besides caffeine that are likely to be

[1] These directions are in part those given by Spencer, *1890 : J. anal. Chem.*, 4, 390.

precipitated by Wagner's reagent,— for caffeine itself is not precipitated by it even in presence of tolerably strong acetic acid. If any absorption of iodine be found in the first portion, then that quantity is to be subtracted from the amount of iodine taken up by the second portion; the difference represents the iodine used up in the formation of the periodide of caffeine. The amount thus used up, multiplied by 0.3834, gives the amount of caffeine in that particular portion of the liquid.

ANN ARBOR, MICHIGAN.

ON THE FORMATION OF ANTIMONY CINNABAR.

BY J. H. LONG.

Received February 15, 1896.

THE composition of the pigment known as antimony cinnabar has been stated by several different formulas, as may be seen by consulting the leading hand-books of chemistry. The substance was usually considered as a mixture of sulphide and oxide or as an oxysulphide with the formula Sb_2S_2O. The formula, Sb_2S_3, is found also in some of the older works, and Baubigny[1] has shown that this is undoubtedly the correct one. Experiments made by myself and described in this Journal, in February, 1895, led me to adopt the same formula.

The compound is usually prepared by boiling a solution of antimony chloride or tartrate with sodium thiosulphate or crude calcium thiosulphate. As obtained from the acid solution of the chloride, the product is not pure and not of constant composition, being frequently mixed with oxychloride. This mixture is a mechanical one and analysis made from it has no value in establishing a formula. The precipitate obtained by boiling a mixture of pure solutions of tartar emetic and sodium thiosulphate, on the other hand as a constant composition, and numerous analyses I have made of it in the past year lead to the formula already given.[2]

By analogy with other formulas established in the paper referred to I suggested there that the reaction between the tartrate and thiosulphate may be represented by this equation:

1 *Compt. rend.*, October 22nd, 1894.

2 *Loc. cit.*

$$2KSbOC_4H_4O_6 + Na_2S_2O_3 + H_2O = 2KNaC_4H_4O_6 + Sb_2O_3 + H_2S_2O_3,$$

the oxide and thiosulphate then acting on each other to form sulphide:

$$Sb_2O_3 + 2H_2S_2O_3 = Sb_2S_3 + 2H_2O + SO_2 + 5O.$$

The oxygen and sulphur dioxide are not liberated as such but held as polythionates with the excess of thiosulphate used.

To throw further light on the reaction I have attempted the formation of the cinnabar by other methods. While the product is sulphide of antimony, it appears that it can be made with its characteristic color only by the decomposition of a thiosulphate. All attempts to obtain the true precipitate by action of hydrogen sulphide or alkali sulphides and sulphur dioxide on antimony solutions failed. The only body formed was the amorphous sulphide, often mixed with sulphur. On the other hand, by the action of a neutral or acid mixture of an antimony compound and a thiosulphate on each other, the cinnabar red product is the only one formed. If the mixture is made alkaline by the addition of a drop or two of ammonia water, no sulphide whatever precipitates. A small amount of hydrated oxide of antimony separates, but the decomposition of the thiosulphate is prevented. On the addition, now, of enough weak acid to neutralize the ammonia a yellow precipitates soon appears, but this speedily changes to deep bright red. The formation of the true cinnabar seems to begin by the appearance of a yellowish intermediate product, which is compatible with the above equations.

In this connection it is interesting to note the behavior of pure antimony trioxide with solutions of thiosulphate. The reaction of the latter with a soluble antimony compound is comparatively rapid, and the experiments were made to show the action of the oxide under the same conditions. It was found that the latter, when added to a strong or weak neutral thiosulphate solution is unable to effect a decomposition, in the cold or by application of heat. When the mixture is boiled the oxide remains perfectly white. This is true even after heating in an autoclave under a pressure of eighteen atmospheres.

It was found, however, that with the addition of a little acid to the mixture of oxide and thiosulphate, a reaction followed after a time, although it never became complete. In a series of experiments a constant weight, 0.576 gram, of the pure precipitated, washed, and dried oxide was taken and mixed with water and a constant weight of sodium thiosulphate in solution, in each case 0.992 gram of the salt. Definite volumes of half normal hydrochloric acid were then added and water enough to make the total volume fifty cc. in each case. The mixtures were made in small Erlenmeyer flasks, loosely stoppered, and were very frequently shaken. The amounts of hydrochloric acid taken are given in the table below. The reactions became apparent only after several minutes, and after five hours, had advanced so far in the mixtures numbered one and two, that the products had become orange. The reactions in the other flasks were less marked, but later became strong. The mixtures were made on October 7th and were shaken many times daily through two months, in fact, as long as any change of color in them was noticed. On December third the amount of sulphide of antimony present was found by the method of Rivot, oxidation by chlorine after preliminary treatment with strong potassium hydroxide solution. The sulphur is found as sulphate and the amount of sulphide formed in each case is shown by the table.

No.	Amount of Sb_2O_5.	$Na_2S_2O_3$.	$\frac{N}{2}$ HCl.	H_2O.	$BaSO_4$ found.	Sb_2O_5 converted.
1	0.576 gram.	0.992 gram.	2 cc.	48 cc.	0.155 gram.	0.064 gram.
2	0.576 "	0.992 "	4 "	46 "	0.293 "	0.121 "
3	0.576 "	0.992 "	8 "	42 "	0.384 "	0.158 "
4	0.586 "	0.992 "	12 "	38 "	0.427 "	0.176 "
5	0.576 "	0.992 "	16 "	34 "	0.454 "	0.187 "

In mixtures one and two no evolution of sulphur dioxide could be detected by the odor or by tests, but in the others it was apparent, weak in 3 and strong in 4 and 5. No free sulphur was precipitated in any case, or at any rate could not be found in the final product. Although but a small part of the oxide was actually converted the color of the products in mixtures 1 and 2, was a deep cinnabar, and perfectly characteristic. The amounts of sulphide formed or of oxide converted are not

proportional to the volumes of acid used, and are much less than should be found on the assumption that the reaction begins by the production of antimony chloride from the oxide. If this were true, the sulphide formed by means of the soluble thiosulphate should increase with the acid taken. The reaction appears to take place between the oxide and thiosulphuric acid liberated by the hydrochloric acid, as was suggested by several experiments. In one case 0.500 gram of antimony oxide was treated with ten cc. of half normal hydrochloric acid and thirty cc. of water, as before, and allowed to stand twenty minutes, with frequent shaking. The mixture was then filtered and to the filtrate one gram of sodium thiosulphate in ten cc. of water was added. In a short time a precipitate of sulphur formed, perfectly light colored, showing the absence of even a trace of the antimony. The rapidity with which the thiosulphate was decomposed showed that the hydrochloric acid taken must be in the filtrate and not in the residue, as oxychloride for instance. Titration of the filtrate showed this in a similar case. In a second experiment the acid and thiosulphate, in amounts equal to those of the last experiment, were mixed, and after the lapse of one minute the now opalescent mixture was added to some antimony oxide. Although the reaction between the first substances had gone into its second stage, showing that the hydrochloric acid was now certainly in combination, a precipitation of antimony sulphide began almost immediately and in a short time the cinnabar color was distinct.

Thiosulphuric acid is usually spoken of as quite unstable, but Landolt has shown[1] that in dilute solutions it may exist many seconds, even minutes. The interval before precipitation is lengthened by dilution. If decomposition begins in presence of compounds of the heavy metals, a sulphide, sulphur dioxide, and polythionates may form. A large excess of thiosulphuric acid is necessary to complete the reaction in this manner, as suggested by the experiments of Vortmann.[2]

In experiment No. 1 of the table above the amount of hydrochloric acid taken is just one-eighth of that necessary to complete this reaction with the thiosulphate:

[1] *Ber. d. chem. Ges.*, **16**, 2958.
[2] *Ber. d. chem. Ges.*, **22**, 2309.

$$2HCl + Na_2S_2O_3 = 2NaCl + H_2S_2O_3.$$

By full conversion enough acid would be liberated to complete the equation assumed at the beginning,

$$Sb_2O_3 + 2H_2S_2O_3 = Sb_2S_3 + 2H_2O + SO_2 + 5O,$$

with the amounts of oxide and thiosulphate taken. It follows, therefore, that not over one-eights of the antimony oxfde taken should be found converted into sulphide, and the result of the experiment shows slightly less than this. According to this theory we should have 0.072 gram of oxide changed. The test shows 0.064 gram. In the second and following experiments the amount of oxide converted is relatively still less. The acid taken in the last experiment is sufficient to decompose all of the thiosulphate and thus permit the conversion of all of the oxide. But the result shows that slightly less than one-third the oxide has been changed. In the first experiments no escape of sulphur dioxide was noticed, while in the last it was quite marked and this fact has doubtless some connection with the low amount of sulphide formed. The reaction which takes place in a weak solution of thiosulphuric acid is evidently different from that in the strong solution, inasmuch as the greater portion of the sulphur seems to be given off as sulphide in the one case and as sulphur dioxide in the other.

In the somewhat similar reaction with arsenious oxide Vortmann[1] suggests this equation,

$$As_2O_3 + 9H_2S_2O_3 = As_2S_3 + 3H_2S_4O_6 + 3SO_2 + 6H_2O,$$

in which but one-sixth of the sulphur present is used to form sulphide. By increasing the amount of hydrochloric acid added to the thiosulphate the decomposition of the latter is hastened.

It is possible that after a time, with increased liberation of sulphur dioxide the formation of sulphide may be retarded, as was suggested by this experiment. I mixed half a gram of the antimony oxide with one gram of sodium thiosulphate in ten cc. of water, and added ten cc. of half-normal hydrochloric acid and thirty cc. of moderately strong solution of sulphur dioxide, free from air. By using water instead of the last solution, precipitation would appear in a few minutes, but in this case it was

[1] *Loc. cit.*

delayed several hours and then but a slight amount of yellowish product appeared. The thiosulphate is therefore protected from decomposition by the presence of the sulphur dioxide.

The cinnabar is easily formed from the oxychloride of antimony without addition of acid. Some recently precipitated and well washed oxychloride was mixed with water and thiosulphate solution of the strength used before. The characteristic color soon appeared and in a short time the whole product seemed to be cinnabar. The reaction is doubtless aided by the hydrochloric acid liberated by the decomposition of the oxychloride in presence of water. The acid in turn attacks the thiosulphate, and so the process becomes continuous and rapid. These reactions are all much hastened by application of heat and the quantitative relations are also altered, but at a temperature of 20° C. thiosulphuric acid seems to be the active precipitating agent in the cases investigated.

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PERHALIDIES OF CAFFEINE.

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Received February 25, 1896.

I. INTRODUCTION.

THE formation of periodides by organic bases has been known as far back as 1839.[1] Their methods of preparation, their composition and properties have been subjects of investigation at different periods since then. Jörgensen,[2] in 1870, made a complete review of the subject, and has contributed a long list of new periodides. In 1887, Gunther[3] made a compilation of all the periodides known up to that time, and reported many new ones. More recently Prescott[4] offered a classification of all know periodides of both organic and inorganic bases, presenting at the same time a history of the principal advances in the study of the subject.

A strict separation of the periodides as such into those of alkylamines and those of pyridine and of its derivatives, seems

1 Bouchardat, 1838: *Compt. rend.*, **9**, 475.
2 *J. prakt. Chem.* [2], **2**, 347, 433, *1870*.
3 *Ann. Chem.* (Liebig), **240**, 66.
4 This Journal, **17**, 775.

hardly necessary. We know of no property, as to composition or stability, which is characteristic of one class of the periodides, and is not shared equally well by the other. At one time, Dittmar[1] thought to have found such a distinguishing reaction in the formation of chloriodides of the bases. According to him, it is only the bases of pyridine structure that are attacked by chloride of iodine, with the formation of chloriodides, RNCl.I. Yet it has been shown[2] previously to his report that this is not the case. Later, Ostermayer[3] reported the formation of such a chloriodide of caffeine, and recently Pictel and Krafft[4] obtained by the action of trichloride of iodine a similar chloriodide of trimethylamine.

All the periodides of primary, secondary, and tertiary ammonium salts, including those of pyridine and its derivatives, contain hydriodic as the salt-forming acid, and the "periodine" is supposed to be linked to the iodine of this acid. The iodine of the acid, being linked directly to the nitrogen of the base, is not affected by reducing agents, such as sulphurous acid, sodium thiosulphate, nascent hydrogen, etc., while the "periodine" is readily attacked under such treatment, and yields hydriodic acid. The constitution of quaternary ammonium periodides, including those of the quaternary pyridine salts, is entirely similar to that of the tertiary class, the hydrogen of the acid being replaced by an alkyl. The following formulas will make this clear:

$R'''N<^{H}_{I.I_n}$, periodides of tertiary ammonium salts.

$R'''N<^{R}_{I.I_n}$, periodides of quaternary ammonium salts.

The organic bases are also capable of forming other halogen additive compounds, besides the simple periodides. These can be classified as follows:

1. Compounds wherein iodine or bromine is linked directly to the nitrogen without the intervention of a halogen acid, such as

[1] *Ber. d. chem. Ges.*, **18**, 162, *1885*.
[2] *J. Chem. Soc.*, **19**, 145, *1866*.
[3] *Ber. d. chem. Ges.*, **18**, 2298, *1885*.
[4] *Bull. Soc. Chim.* [3], **7**, 72, *1892*.

pyridine tetraiodide, $C_5H_5N.I_4$,[1] quinoline tetrabromide, $C_9H_7N.Br_4$.[2]

2. Those obtained by the action of monochloride[3] and trichloride[4] of iodine upon bases. They contain both chlorine and iodine linked directly to the nitrogen. Their structure can be represented by the general formula $R'''N<^{Cl}_{I}$. These compounds still retain the power of forming salts by union with acids, as $(R'''NClI).HCl$.

3. Periodides wherein the "periodine" is linked to another halogen not iodine. These are few in number, and are all on the quarternary ammonium type, $R'''N<^{R}_{Br.I_n}$.

4. Periodides containing another acid[5] in addition to hydriodic acid, such as in herapathites, periodo selenites, phosphates, chlorides, etc. But as each contains hydriodic acid, Jörgensen legitimately infers that the "periodine" is, in all probability, linked to this acid and not to the other.

5. Perbromides of the hydrobromide of bases. Only very few of these have been reported, although it is well known that a great number of alkaloids are precipitated by bromine dissolved in hydrobromic acid. Pyridine,[6] quinoline,[7] and nicotine[8] form such perbromides.

All the perhalides of organic bases, so far reported, (except the simple periodides) can be referred to one of these five classes. And yet it can hardly be doubted that periodides and perbromides of other salts than hydriodides and hydrobromides respectively, are capable of existence. I have not been able to find any reports upon periodides in which either hydrochloric or hydrobromic acid has exactly the same function as hydriodic acid has in the simple periodides. Such derivatives can only be prepared when precautions are taken to strictly insure the absence of hydriodic acid during the preparation of the periodide,

[1] Dafert, *Monatsh. Chem.*, **4**, 509, *1883*; Prescott and Trowbridge: This Journal, **17**, 865.
[2] Grimaux, *1882*: *Bull. Soc. Chim.*, **58**, 124.
[3] Dittmar, *1885*: *Ber. d. chem. Ges.*, **18**, 162.
[4] Pictel and Krafft: *loc. cit.*, 72.
[5] Jörgensen, *1876*: *J. prakt. Chem.* [2], **14**, 213, 356; **15**, 65.
[6] Grimaux: *Bull. Soc. Chim.*, **38**, 127, *1882*.
[7] *Ber. d. chem. Ges.*, **19**, 2766, *1886*.
[8] *Ann. Chem.* (Liebig), **131**, 260.

and this has never been the case in the methods that have hitherto been employed for that purpose. In the following pages will be found a description of such periodides of caffeine, which have been obtained by a method different from those that have been described. The compounds have all been prepared by substituting chloroform for alcohol as the medium of reaction, thus eliminating the action of iodine upon alcohol at higher temperatures, and the subsequent formation of hydriodic acid. Not only periodides, but perbromides of similar composition and constitution have been prepared by this method. The method is, indeed, of very general application for such purposes. Periodides of hydrobromides and hydrochlorides of the following bases have thus been obtained: Quinine, quinidine, cinchonine, cinchonidine, strychnine, brucine, atropine and quinoline (of the hydrobromide only).

It has been said of the periodides that "if they contain, as their behavior has been interpreted to imply, for every atom of iodine that is linked to the base, a number of atoms of iodine linked only to iodine, they offer a striking example of the influence of a basal group upon iodine atoms to which it is not linked." This naturally suggested the question, whether this influence is or is not proportional to the basal power of the group; in other words, is the number of iodine atoms thus attached under given conditions, as index of the basic power of the different bases? Again, we might ask whether the same influence is exerted in the same degree upon bromine. And furthermore, we might inquire, in how far does the nature of the halogen acid modify the influence of the base upon the "periodine," or "perbromine?" The following pages give an account of such a comparative study of perhalides of one base, caffeine.

II. PERIODIDES OF CAFFEINE.

Caffeine Hydriodide Diiodide, $C_8H_{10}N_4O_2.HI.I_2$.—Tilden reported in 1865,[2] that when a solution of caffeine in dilute alcohol, containing some hydriodic acid, is exposed to sunlight, there appears in a few days a deposit of beautiful crystals, with a metallic greenish appearance, unstable, readily decomposing

[1] Prescott, 1885: This Journal, **17**, 775.
[2] *J. Chem. Soc.*, **18**, 99.

even at the water-bath heat. He assigned to the compound the formula $(C_8H_{10}N_4O_2.HI.I_2)_2.3H_2O$, and this agress closely with the results of his analysis. In repeating the experiment, I find that under certain conditions a diiodide is formed, but the results of my analysis show no water of crystallization. Again, the diiodide is formed only when the formation of the crystals is tolerably rapid, as when the solution is kept in a warm place and exposed to direct light, conditions favoring oxidation of hydriodic acid. If, however, the liberation of iodine be very slow, yielding about a half gram of periodide in six or seven weeks, a tetraiodide is produced. The diodide, obtained as above described, was filtered on a pump, washed with water containing some hydriodic acid, dried on porous plates and finally over sulphuric acid *in vacuo*. The samples were analyzed for total iodine and for the "periodine," or, as Tilden calls it, the "exterior" iodine. The first is estimated by suspending a weighed sample in water, treating with a solution of sulphur dioxide, then precipitating with silver nitrate and nitric acid. The "periodine" is estimated by titrating with a standard solution of sodium thiosulphate. The difference between the total and "exterior" iodine is that which corresponds to the hydriodic acid. Two independent samples thus prepared gave the following results:

	Calculated for $C_8H_{10}N_4O_2.HI.I_2$.	Found. I.	II.
Total iodine	66.06	65.12	64.29
Periodine	44.04	44.04	44.18

The diiodide consists of long hexagonal prisms, with a metallic greenish luster. It decomposes readily when moist, but is quite stable when dry. When suspended in water the crystals lose their luster and become coated with a brown-red layer of the tetraiodide. It is soluble in warm alcohol with decomposition, insoluble in ether and chloroform. It melts at 171° C.

Caffeine Hydriodide Tetraiodide, $C_8H_{10}N_4O_2.HI.I_4$.—This is the periodide which caffeine usually forms when it forms any at all, except as above described. It is the most stable periodide of caffeine, and is formed under many different conditions, in both the amorphous and crystalline state. It has been obtained by the following methods:

1. When a solution of caffeine is treated with a solution of iodine in potassium iodide (Wagner's reagent), there is no visible reaction. On the addition of some mineral acid, a heavy amorphous dark-red precipitate is at once thrown down. The precipitation of caffeine in this way is quantitative, and forms the basis of a method for the estimation of caffeine.[1] The composition of this precipitate is, as I have fully described,[2] $C_8H_{10}N_4O_2.HI.I_4$. It was obtained for analysis in many different ways by varying the relative quantities of the reagents employed, but it has always proven to be of the same composition. The samples for analysis were obtained by filtering the amorphous precipitate on a pump, washing with water to remove the potassium salts, drying rapidly on porous plates, and finally *in vacuo* over sulphuric acid. The following are the results of analysis:

	Calculated for $C_8H_{10}N_4O_2.HI.I_4$.	Found. I.	II.	III.	IV.
Total iodine.....	76.43	75.12	75.66	75.84	....
Periodine	61.15	60.79	60.11	60.81	60.76

2. When caffeine is dissolved in chloroform and is treated with a solution of iodine also in chloroform, no formation of any periodide could be noticed, even when the mixture is allowed to stand for weeks. If into this solution dry hydriodic acid gas be now passed, there is at once precipitated an amorphous dark-red periodide, identical in composition with that described under 1. Upon analysis it gave the following figures:

	Per cent.
Total iodine.....	75.14
Periodine	60.23

3. When a solution of caffeine in hydriodic acid is exposed to sunlight, but the liberation of iodine is hindered either by low temperature, or the presence of some reducing agents in the solution, then the crystals that are formed have the composition of the tetraiodide, and not that of diiodide. They also have a different appearance, being short prisms of a deep blue color. Several samples obtained in this way furnished the following figures:

[1] This Journal, 18, 331.
[2] *Loc. cit.*

	I.	II.	III.	IV.
Total iodine	....	....	....	75.11
Periodine.....	60.26	59.86	59.75	60.60

4. When either caffeine hydrobromide dibromide or tetrabromide is triturated with a solution of potassium iodide in water, there is again produced the same amorphous periodide. It gives upon analyses 59.90 per cent. "of exterior" iodine.

These four different methods show the great tendency of caffeine to form the higher periodide, which is apparently more stable than the diiodide. Weak base as it is, caffeine readily forms a higher periodide than is produced under similar conditions by many other organic bases.

Properties.—The periodide in the amorphous state and when dry, is of a dark blue-red color. It is quite stable when dry, and can be heated at 100° C. for many days without any appreciable loss of iodine. When moist it readily gives off iodine. Suspended in water, it gives up sufficient iodine to saturate the liquid, and after that remains unchanged. A solution of potassium iodide removes only a little more iodine than pure water alone. The periodide cannot be recrystallized from alcohol without considerable decomposition into caffeine and iodine. It is more soluble in methyl alcohol, and if not too much heat be used in dissolving it, the periodide can be obtained unchanged on spontaneous evaporation of the alcohol in the form of dark-blue needles. Ethyl acetate is, however, the best solvent for this periodide, as the latter dissolves in acetic ether without decomposition, even when heated. On cooling, the periodide separates in fine compact crystals. It is insoluble in chloroform, ether, benzene and carbon disulphide. It melts at 215° C.

Caffeine Hydrobromide Tetraiodide, $C_8H_{10}N_4O_2.HBr.I_4$.—Caffeine forms with hydrobromic acid a salt of the following composition, $C_8H_{10}N_4O_2.HBr + 2H_2O$.[1] The salt can best be obtained in a pure state by passing dry hydrobromic acid gas into a solution of caffeine in chloroform. The white crystalline precipitate is filtered, washed with chloroform, and dried in an atmosphere free from moisture. Thus prepared it has the composition $C_8H_{10}N_4O_2.HBr$. The periodide of this hydrobromide

[1] E. Schmidt, *1881: Ber. d. chem. Ges.*, 14, 815.

can only be prepared in the absence of other halogen acids, especially of hydriodic acid. Therefore the addition of iodine as a solution in potassium iodide, to a solution of caffeine hydrobromide, is out of the question, as in such a case the periodide of the hydriodide will be formed. Nor can alcohol be successfully employed as a solvent for iodine, because this will furnish hydriodic acid, and also because the periodide of the hydrobromide itself is more or less dissociated by alcohol. This periodide is, however, readily obtained when a slow stream of dry hydrobromic acid gas is led into a solution of caffeine and iodine in chloroform. The addition of the acid must be very slow, and care must be taken to have the iodine in excess, otherwise the pure hydrobromide, or lower periodides of it will be thrown down together with the tetraiodide. In such cases redigesting the mixed periodides in a fresh solution of iodine in chloroform converts them into the tetraiodide. Further digestion shows no absorption of iodine. The periodide is filtered, washed with chloroform to remove the excess of caffeine or iodine, as the case may be, dried on porous plates, and finally in a desiccator. The "exterior" iodine is estimated by titration with sodium thiosulphate. The bromine is found by subtracting from the total mixture of silver halides, as obtained by precipitation with silver nitrate, the quantity of silver iodide corresponding to the "periodine" as found by titration. This difference represents the amount of silver bromide. The accuracy of this method was tested in several instances by actually estimating the amount of silver as such in the precipitate of the mixed halides, and from this the relative proportions of the two halogens were calculated.

The analysis of several samples furnished the following figures:

	Calculated for $C_8H_{10}N_4O_2.HBr.I_4$.	Found. I.	II.	III.
Iodine	64.79	63.56	63.91	62.28
Hydrobromine	10.37	9.63	....	....

This periodide is usually obtained as an amorphous powder. But when the addition of hydrobromic acid is very slow, it can be obtained in microscopic crystals. It is of a dark-brown chocolate color, and melts at 183° C. It is decomposed by water

but slowly, more readily, however, than the corresponding hydriodide. It dissolves readily in alcohol, with considerable decomposition. It is more soluble in methyl than in ethyl alcohol, and also with less decomposition. On evaporating the methyl alcohol the tetraiodide can be obtained in brown crystals. It can also be recrystallized from ethyl acetate. Ether removes considerable iodine, and chloroform, hot or cold, does not affect it. On exposure to air the periodide gradually, but slowly, loses iodine, and hardly any if protected from moisture. By heating to 100° C. the iodine can be driven off completely. Thus this periodide is in all respects a less stable compound than the corresponding tetraiodide of caffeine hydriodide.

Caffeine Hydrochloride Diiodide, $C_8H_{10}N_4O_2.HCl.I_2$.—Caffeine is capable of uniting with hydrochloric acid under certain conditions, and the salts have been assigned the following composition: $C_8H_{10}N_4O_2.HCl + 2H_2O$ and $C_8H_{10}N_4O_2.2HCl$.[1] Pure caffeine hydrochloride is however much easier obtained by simply passing dry hydrochloric acid gas into a solution of caffeine in chloroform. Washed with chloroform, and dried in an atmosphere free of moisture, it has the composition $C_8H_{10}N_4O_2.HCl$.

Compounds containing both chlorine and iodine have been reported before. Tilden[2] obtained a chloriodide of caffeine by the action of chloride of iodine upon caffeine. It combines with acids to form salts, and Tilden assigns to it the composition $C_8H_{10}N_4O_2.Cl_2I$, or $C_8H_{10}N_4O_2ICl.HCl$. But from Dittmar's[3] latest reports upon the action of chloride of iodine upon bases in general, the caffeine compound most likely has the composition as expressed by the second formula. The periodide presently to be described is however the first periodide of caffeine wherein the hydrochloric acid has the same function in the molecule as hydriodic acid usually has in the other periodides. And, to my knowledge, this is the first periodide of its kind ever reported of any base. The "periodine" in the hydrobromide is linked to the nitrogen through the bromine; in the periodides of the hydrochloride it is linked through the chlorine.

Caffeine hydrochloride diiodide is prepared by passing hydro-

[1] E. Schmidt: *Ber. d. chem. Ges.*, **14**, 815.
[2] *J. Chem. Soc.*, **19**, 145.
[3] *Ber. d. chem. Ges.*, **18**,162.

chloric acid gas into a solution of caffeine into chloroform containing iodine. The periodide separates almost immediately in the form of compact, small, crystalline granules, of light-brown to brown color. The samples for analysis were prepared similarly to the other periodides described, and furnished the following results:

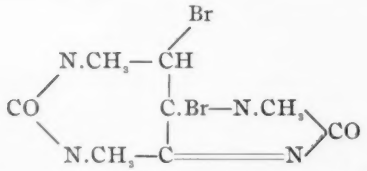
	Calculated for $C_8H_{10}N_4O_2.HCl.I_2$.	Found. I.	II.	III.	IV.	V.
I	52.34	53.38	52.44	53.44	52.88	53.64
HCl	7.53	7.40	....	....	....	....

The periodide is of a light brown color, crystalline, and melts at 165° C. Digested with excess of iodine for several days, it refuses to take up any more iodine. It is rapidly decomposed by water. Both methyl and ethyl alcohol remove the iodine readily and completely, leaving a white powder of caffeine hydrochloride. The periodide is soluble in ethyl acetate with partial decomposition, is insoluble in either cold or hot chloroform, and is not affected by ether. Exposed over potassium hydroxide in a desiccator it remains unchanged, but slowly loses iodine when exposed to air not freed from moisture. On heating to 100° C. all the iodine is driven off. Thus in all its properties it is even less stable than the periodide of caffeine hydrobromide.

III. PERBROMIDES OF CAFFEINE.

The action of bromine upon caffeine has been the subject of investigation many times. When pure bromine is employed, in absence of water, the final action of bromine results in the formation of a substitution product, bromocaffeine, $C_8H_9BrN_4O_2$.[1] In presence of water the action of bromine upon caffeine is for the most part that of an oxidizing agent, as has been shown by Maly and Hinteregger.[2] But under whatever conditions bromine is added to a solution of caffeine or to the dry base, be it as bromine-water or pure bromine, there is at first thrown down an orange-red to a brick-red precipitate. According to Maly and Hinteregger's results of analysis it is a mere addition product, caffeine dibromide, and E. Fisher[3] expresses the same opinion. The constitution of the compound is presumably this:

[1] O. Schultzen: *Ztschr. Chem.*, *1867*, 614: E. Fisher: *Ann. Chem.* (Liebig), **215**, 264.
[2] *Monatsh. Chem.*, **3**, 85, *1882*.
[3] *Ann. Chem.* (Liebig), **215**, 264.



I have subjected caffeine to the action of bromine under many varied conditions, but in no case have I been able to obtain this addition product. Indeed, as will be shown, its existence is entirely hypothetical. Although Maly and Hinteregger's results of analysis agree with the theoretical figures of the formula assigned by them to the compound, yet their method of obtaining and purifying the substance for analysis is such, as to preclude the reliability of the results of analysis. The addition compound will be shown to have the composition $C_8H_{10}N_4O_2$.$HBr.Br_4$, and not $C_8H_{10}N_4O_2.Br_6$. This perbromide loses a portion of its bromide quite readily; consequently, it must be analyzed, or at least protected from exposure, as soon as dry. Hence, Maly and Hinteregger's results, obtained upon samples which have been previously exposed over lime in a desiccator for several weeks, cannot furnish reliable data as to the composition of the original substance. Just as under the action of iodine in presence of hydriodic acid, caffeine exhibits a great tendency to form higher periodides, so under the action of bromine it always forms the tetrabromide of the hydrobromide. This takes place whether hydrobromic acid be added as such or not. When none is added, some hydrobromic acid is produced, either by the action of bromine upon water or by the direct action upon caffeine,

$$C_8H_{10}N_4O_2 + Br_2 = C_8H_9BrN_4O_2 + HBr.$$

It is only under special conditions that lower perbromides of caffeine are obtained.

Caffeine Hydrobromide Tetrabromide, $C_8H_{10}N_4O_2.HBr.Br_4$.—Whenever bromine is allowed to act upon caffeine, this perbromide is one of the first products of the reaction, if not the only one. It is produced in presence or in absence of hydrobromic acid, in presence of water, of chloroform, or when pure bromine is employed.

1. *In Presence of Water.*—When bromine-water is gradually added to a solution of caffeine acidulated with hydrobromic acid, there is produced a yellow amorphous precipitate, which becomes darker, and more compact; also, if the addition of bromine be very gradual, the precipitate becomes crystalline. The same compound is however obtained easier, and more crystalline, by the following method of procedure: A stream of carbon dioxide is allowed to bubble through a column of pure bromine. and the fumes of the latter, greatly diluted with carbon dioxide, are carried into a solution of caffeine containing some hydrobromic acid. As the bromine first reaches the solution, the bubble of the gas becomes surrounded with a pale-yellow film, which soon grows darker, and the product finally settles to the bottom as an orange-red crystalline deposit, consisting of distinct small prisms. If the bromine fumes be passed into the solution too rapidly, the resulting product is amorphous. One gram of caffeine furnishes by this method two and three-tenths grams of the perbromide, which is about eighty per cent. of the theoretical value. The samples for analysis were filtered, by the use of a pump, washed with weak bromine-water, and dried by pressing on very porous plates. When dry, in about two hours, the upper layer of the mass is removed, and the rest is put away in small glass-stoppered bottles, where it remains unchanged for weeks. The washing and drying should not be prolonged any more than is necessary, as the compound loses bromine readily, especially when moist and exposed to open air. The samples were analyzed for the "exterior" bromine and for total bromine. The first was estimated by suspending a weighed quantity of the sample in a solution of potassium iodide, and the iodine thus liberated is titrated with a standard solution of sodium thiosulphate. The total bromine was estimated by precipitation with silver nitrate, in a manner entirely similar to that employed in the estimation of total iodine in the periodides. Several samples, prepared separately, gave the following results:

	Calculated for $C_8H_{10}N_4O_2.HBr.Br_4$.	Found. I.	II.	III.	IV.	V.	VI.
Total bromine.....	67.23	67.37	65.74	67.89	....	....	....
"Perbromine".....	53.78	54.00	52.07	54.04	54.18	53.11	52.58

The addition of hydrochloric acid or sulphuric acid, instead of

the hydrobromic, does not give perbromides of salts of these acids, but the same perbromide of the hydrobromide of caffeine.

The same product is obtained even if no acid whatever be added. Thus, when fumes of bromine, absolutely free from hydrobromic acid, are passed into a solution of caffeine, there appears after a short time a precipitate of exactly the same appearance and composition as the perbromide described above. The precipitation is much slower than when hydrobromic acid is present, nor is the yield so large. One gram of caffeine yields from two-tenths to three-tenths gram of the perbromide, which is only about eight to ten per cent. of the theoretical value. Samples for analysis, prepared as previously described, gave the following figures:

	I.	II.	III.
Total bromine	65.92	....	....
"Perbromine"	52.57	53.27	54.75

This is undoubtedly the same perbromide as obtained in presence of hydrobromic acid. The slow precipitation and the small yield point conclusively that a large portion of the caffeine suffers some other changes, namely, those of oxidation and substitution, either of which would give rise to hydrobromic acid. The acid thus produced would at once tend to form the perbromide of the hydrobromide of caffeine. Filtrates from such perbromides invariably give within a short time bulky precipitates of the white bromocaffeine, $C_8H_9BrN_4O_2$.

Great precautions were taken to insure the absence of hydrobromic acid in the bromine used. For this purpose the latter was washed with a solution of sodium hydroxide, then with sulphuric acid, and finally kept under a column of sulphuric acid saturated with silver sulphate. In some experiments the fumes were also passed through a second bottle containing sulphuric acid and silver sulphate. But the perbromide of the hydrobromide was always produced even under these conditions

Properties.—The perbromide consists of small orange-red prismatic crystals. It melts sharply at 170° C. with previous decomposition into the dibromide, and finally decomposes completely. When suspended in water, it gives up some of its bromine, and then gradually and slowly changes into the white bromocaffeine.

Two grams of the perbromide change in this way completely in about one week. When spread out on plates and exposed to air for about twenty-four hours, it loses two atoms of bromine, leaving a more stable residue, the corresponding dibromide, which suffers very little loss of bromine on further exposure. The tetrabromide is quite soluble in alcohol, more so when warm, from which it separates, on cooling, in the form of a lower perbromide mixed with some pure caffeine. Methyl alcohol dissolves the tetrabromide very readily, with the production of large quantities of formic aldehyde, and almost complete reduction of the bromine. It dissolves in warm ethyl acetate, and this on evaporation furnishes yellow crystals of a lower perbromide. The perbromide is only slightly soluble in either hot or cold chloroform. Ether removes two atoms of bromine, leaving the yellow dibromide of caffeine hydrobromide. When heated, the tetrabromide loses a portion of its bromine, and finally changes into bromocaffeine, especially at a higher temperature, about 160°–170° C.

2. *Action of Bromine in the absence of Water.*—When a weak solution of bromine in chloroform is added to a solution of dry caffeine in the same solvent, there appears after some hours' standing a deposit of flaky crystals. With strong solutions of bromine the formation of crystals begins to take place at once, the amount constantly increasing. The mother liquids, after filtering off the crystals, give new crops of the same compound. It was the compound thus produced that was analyzed by Maly and Hinteregger, after being allowed to stand several weeks over lime. The perbromide was filtered, washed with chloroform containing bromine, and dried on porous plates. It was found to be identical in composition with the one obtained similarly but with the previous addition of hydrobromic acid gas also dissolved in chloroform. The analyses I. and II. are upon samples obtained without the use of hydrobromic acid, while analyses III. and IV. are upon samples prepared with the addition of the acid.

	I.	II.	III.	IV.
Total bromine	68.25	....	....	....
Perbromine	52.25	54.79	54.40	52.82

The perbromide thus obtained is entirely identical in its behavior towards different reagents and solvents with that obtained by the action of bromine upon caffeine in presence of water. It melts at 170° C.

The question may be asked, whence comes the hydrobromic acid that furnishes the hydrobromide of the base? The bromine used in all these experiments was carefully freed from any hydrobromic acid that might have been originally present. The chloroform also was dehydrated for several days over fused calcium chloride, and finally carefully distilled. Blank experiments with absolutely dry chloroform (distilled over phosphorus pentoxide) have established that there is practically no absorption of bromine by the chloroform, when at three per cent. solution of the halogen in that liquid is exposed to light for several days. Therefore, the hydrobromic acid in the reaction could not have been produced from the substituting action of bromine upon chloroform, a reaction which takes place only at higher temperatures. From the rapid formation of the perbromide when strong solutions of bromine are used, it may reasonably be assumed that at least a portion of the hydrobromic acid, if not all of it, must have been produced directly as one of the products of the substituting action of bromine upon caffeine itself, thus:

$$C_8H_{10}N_4O_2 + Br_2 = C_8H_9BrN_4O_2 + HBr.$$

Additional proof to this theory is lent by the fact that by fractional precipitation, products are eventually obtained which give somewhat higher results for total bromine, while the "perbromine" is about the same. This would point towards the formation of $C_8H_9BrN_4O_2.HBr.Br_2$, a compound, the description of which will be given further on. The last crops of crystals show also a lower melting-point, 150°–156° C.; and when the crystals are suspended in water and treated with sulphurous acid, they yield besides caffeine an insoluble precipitate of the white bromocaffeine.

3. *Action of Pure Bromine.*—When dry caffeine is slowly added to pure bromine the first portions go into solution, but further addition produces a dark-red insoluble mass, which was supposed by Maly and Hinteregger, and by E. Fisher, to be the

caffeine dibromide, $C_8H_{10}N_4O_2.Br_2$. It is, however, not that, but the same tetrabromide of caffeine hydrobromide just described, mixed with a similar perbromide of bromocaffeine.

Dry caffeine was slowly added to a large excess of bromine free from hydrobromic acid, and the mixture was allowed to stand six hours. The thick dark mass was then spread out on porous plates, and allowed to remain over lime for three days. It was then divided into three portions: (*a*) was analyzed at once, (*b*) was washed with chloroform, and (*c*) was again redigested in pure bromine. The results of analysis are as follows:

	a.	*b.*	*c.*
Total bromine	69.45	68.50	68.03
Perbromine	53.88	54.60	53.07

On treatment with reducing agents there is left a slight residue of the insoluble bromocaffeine, and its formation would readily account for the high results of total bromine. The reaction then in this case is the same as when chloroform is employed. A small portion of the caffeine is at once attacked by the bromine and forms bromocaffeine and hydrobromic acid. The acid at once unites with the unchanged caffeine and forms the insoluble perbromide, thus protecting it against further direct action of bromine; then the bromocaffeine is in its turn slowly changed into a similar perbromide.

So far, then, as experimental evidence goes, the caffeine dibromide, $C_8H_{10}N_4O_2.Br_2$, is entirely hypothetical. It may still be said that the evidence does not exclude the possibility that only two atoms of bromine go to form the perbromide, while the other two atoms are retained by caffeine through the unsaturated lining between the two carbon atoms. Against this view there stands the simple fact that iodine, even in dilute solutions in water, forms the analogous tetraiodide. It is hardly probable that iodine would attach itself so readily to carbon. Then again, no assimilation of either bromine or iodine by caffeine takes place unless some acid be present. Hence, the constitution of this perbromide must be analogous to that of the periodide, *i. e.*, it is a pure and simple caffeine hydrobromide tetrabromide.

Caffeine Hydrobromide Dibromide, $C_8H_{10}N_4O_2.HBr.Br_2$.—When the tetrabromide is exposed to air it loses bromine, and after

twenty-four to forty hours there is left a yellow amorphous powder, which is tolerably stable and can be further exposed for many days without any appreciable loss of bromine. The results of analysis show this to be caffeine hydrobromide dibromide. The same compound is obtained by treating the tetrabromide with anhydrous ether. Samples of the tetrabromide were finely powdered under ether, and the digestion with ether was continued until fresh portions of the solvent showed no coloration when added to the perbromide. The yellow residue was filtered, washed with ether, and dried by exposure. It is identical in composition and properties with that obtained by simple exposure of the tetrabromide. Analyses I, II, and III are upon samples obtained by exposing the tetrabromide to air. Analyses IV and V are upon samples obtained by treatment with ether.

	Calculated for $C_8H_{10}N_4O_2.HBr.Br_2$.	Found. I.	II.	III.	IV.	V.
Total bromine	55.17	....	53.45	....	54.99	....
Perbromine	36.78	36.48	35.50	35.93	36.87	35.83

The dibromide ranges in color from pale-yellow to a decided yellow. It is amorphous, and melts at 170° C. When suspended in water it turns orange-red, and, as analysis shows, is changed into the tetrabromide. It is soluble in ethyl alcohol with less decomposition than the higher perbromide. On cooling the alcohol it separates in distinct tetrahedral crystals, containing less bromine than the original compound (total = 42.50 per cent., and "exterior" bromine 27.8 per cent.) Methyl alcohol dissolves the dibromide even more readily than ethyl alcohol, also with less decomposition than it does the higher perbromide. It is slightly soluble in ethyl acetate, insoluble in chloroform and ether. It remains tolerably permanent when heated to 100° C., but, on prolonged heating, or at higher temperature, it is rapidly converted into bromocaffeine.

Caffeine Hydrochloride Tetrabromide, $C_8H_{10}N_4O_2.HCl.Br_4$.— The preparation of this perbromide requires many precautions, for otherwise the product is impure, being mixed with the perbromide of the hydrobromide. First of all, the bromine must be perfectly free from hydrobromic acid, and the chloroform must be free from alcohol and moisture. Second, a dilute solu-

tion of bromine must be employed, so dilute that the addition of it to caffeine should produce no precipitation of the perbromide of caffeine hydrobromide within at least one-half hour. When all these conditions are observed, the perbromide of the hydrochloride is readily obtained by passing a stream of dry hydrochloric acid gas into a dilute solution of caffeine and bromine in chloroform. It separates in compact red crystals. The acid must be passed into the solution very slowly to prevent the formation of pure caffeine hydrochloride; care must also be taken to replace the bromine as it is gradually being used up, avoiding, however, a large excess of it at any time. The substitution of carbon tetrachloride for chloroform will not answer, for although caffeine is so readily soluble in the latter, it is almost insoluble in the former. Samples were washed with chloroform, dried in the usual manner, and analyzed for the exterior bromine and for hydrochloric acid. The latter was estimated by subtracting from the total weight of the mixed silver halides the quantity of silver bromide corresponding to the bromine as found by titration with sodium thiosulphate. The analysis furnished the following figures:

	Calculated for $C_8H_{10}N_4O_2.HCl.Br_4$.	Found. I.	II.	III.
Bromine	58.14	56.75	56.70	56.00
HCl	6.61	6.98	....	....

This compound is of a somewhat lighter color than the corresponding hydrobromide. The crystals, when examined under the microscope, present the appearance of the distinct prisms. The perbromide melts at 149° C. sharp. Suspended in water, it remains unchanged for a time, then decomposes, and finally yields bromocaffeine. Methyl and ethyl alcohol, as well as ether, convert it into caffeine hydrobromide dibromide. Exposed to air, it loses bromine more rapidly than the corresponding tetrabromide of the hydrobromide. On gentle warming for two or three days it still retains a decidedly yellow color.

IV. PERHALIDES OF CHLOROCAFFEINE.

It appears from the results which have been presented that caffeine, although a weak base, forms tolerably stable and rather high perhalides. I have next attempted to prepare perhalides

of chloro- and bromocaffeine, and compare these with those of caffeine itself. One would judge, *a priori*, that the introduction of such strong negative elements as chlorine and bromine into a weak base, would greatly weaken its tendency to form perhalides. And yet, experience shows that the halogen substitution derivatives of caffeine are still capable of forming definite salts, and that they also form even higher perhalides than caffeine itself.

Chlorocaffeine Hydriodide, $C_8H_9ClN_4O_2.HI$.—This salt can only be prepared in absence of water. Chlorocaffeine, prepared according to E. Fisher's[1] method, is dissolved in chloroform, and a stream of dry hydriodic acid gas is passed into the solution. The salt soon separates in the form of white heavy crystals. These are filtered, washed with chloroform, dried first by exposure and finally over solid potassium hydroxide. The acid was estimated by suspending a weighed quantity in water and titrating with a twentieth-normal solution of potassium hydroxide, using phenolphthalein as an indicator.

	Calculated for $C_8H_9ClN_4O_2.HI$.	Found.
HI	35.82	35.69

The salt is decomposed at once by water and alcohol. It gives up its hydriodic acid when exposed to air, probably through absorption of moisture, for when kept over potassium hydroxide for twenty hours it still contains 35.45 per cent. of hydriodic acid.

Chlorocaffeine Hydrobromide, $C_8H_9ClN_4O_2.HBr$.—This salt is prepared similarly to the hydriodide. It is, however, less stable and loses its acid more readily. Analysis gives the following figures:

	Calculated for $C_8H_9ClN_4O_2.HBr$.	Found.
HBr	26.18	26.80

Kept over potassium hydroxide for ten hours it showed only 24.80 per cent. of hydrobromic acid.

Chlorocaffeine Hydrochloride, $C_8H_9ClN_4O_2.HCl$.—This salt is still less stable than the hydrobromide. It is necessary to wash it with chloroform saturated with hydrochloric acid, and dry for analysis as rapidly as possible.

[1] *Ann. Chem.* (Liebig), 215, 262.

	Calculated for $C_8H_9ClN_4O_2.HCl$.	Found.
HCl	13.75	12.92

Kept over potassium hydroxide for 6 hours it showed only 6.15 per cent. of hydrochloric acid.

Chlorocaffeine Hydriodide Pentiodide, $C_8H_9ClN_4O_2.HI.I_5$.—Chlorocaffeine is dissolved in chloroform and is mixed with a solution of iodine in the same solvent. A slow stream of dry hydriodic acid gas is now passed into the mixture. A black amorphous powder separates at once. This is finely powdered and redigested with a fresh solution of iodine in order to insure complete reaction. If it had been previously completed, no further absorption of iodine will take place. The periodide is filtered, washed with chloroform, and dried in the usual manner. The "periodine" is estimated by titration with sodium thiosulphate. The total iodine is estimated by subtracting from the mixed silver halides (by Carius' method) the quantity of silver chloride which corresponds to the chlorine in the chlorocaffeine. The results of analysis are as follows:

	Calculated for $C_8H_9ClN_4O_2.HI.I_5$.	Found.		
		I.	II.	III.
Total iodine	76.78	76.15	....	....
Periodine	63.99	63.08	62.66	62.75

This periodide is a black amorphous powder with a slightly bluish tint. It melts at 185°–6° C. It is decomposed by water, alcohol, more readily by methyl alcohol, by ether and ethyl acetate, giving in all cases the white chlorocaffeine. It is slightly soluble in chloroform. Washing the periodide with a large amount of chloroform does not diminish the per cent. of the halogen in the compound. When exposed to air it shows only slight signs of alteration, and even on heating the periodide at 100° C. for twenty-four hours, only a portion of the iodine can be driven off.

Chlorocaffeine Hydrobromide Pentiodide, $C_8H_9ClN_4O_2.HBr.I_5$.—This periodide is prepared by the same method as the periodide just described, substituting hydrobromic for hydriodic acid. If the acid be passed rapidly, the periodide comes down amorphous; if slowly, it assumes a crystalline appearance. Redigestion in a fresh solution of iodine shows no increase in the per cent. of

iodine in the periodide. On being washed with pure chloroform the periodide suffers no appreciable loss of the halogen. It was analyzed with the following results :

	Calculated for $C_8H_9ClN_4O_2.HBr.I_5$.	Found. I.	II.	III.
Iodine	67.15	65.5	67.07	66.29
HBr	8.49	....	8.21	....

The hydrobromic acid was estimated by subtracting from the mixed silver halides (by Carius' method) the quantities of silver chloride and iodide which correspond to the chlorine of chlorocaffeine, and to the iodine as found by titration respectively.

In appearance this periodide is not quite as black as the periodide of the hydriodide. It melts at 169° C. It is however far less stable than the hydriodide, giving up its iodine very readily to water, alcohol, ether, and ethyl acetate ; somewhat soluble in chloroform. When exposed to air it loses its iodine very rapidly, and on gentle warming leaves pure chlorocaffeine. It is even more unstable than the periodide of the hydrochloride of chlorocaffeine, an irregular gradation of stability as compared with that of the periodides of caffeine itself.

Chlorocaffeine Hydrochloride Tetraiodide, $C_8H_9ClN_4O_2.HCl.I_4$. —The preparation of this compound has been attended with some difficulties, because of its greater solubility in chloroform than the other periodides. The results of analysis by themselves would not entirely justify the formula of the compound as given, had it not been supported by the analysis of the far more stable periodide of bromocaffeine hydrochloride, which certainly has the analogous constitution. Washed with chloroform and dried, this periodide furnished upon analysis these figures :

	Calculated for $C_8H_9ClN_4O_2.HCl.I_4$.	Found. I.	II.	III.
Iodine	70.49	72.70	70.28	73.51 (?)

This periodide is of a blue-black color, and is crystalline. It melts at 137° C. It is decomposed by the different reagents similarly to the other periodides. It is however more stable than the periodide of the hydrobromide, losing iodine only very slowly on exposure to air. When gently heated it takes several hours to drive off all the iodine from a small sample of the periodide.

Chlorocaffeine Hydrobromide Pentabromide, $C_8H_9ClN_4O_2.HBr.Br_5$.—When a solution of chlorocaffeine in chloroform is treated with bromine and set aside, there appear within twenty-four hours long beautiful red crystals. The more bromine added, the quicker and more abundant is the crop; if quite a strong solution of bromine in chloroform be employed, the crystals appear within ten to fifteen minutes. On the other hand, the more carefully the bromine and chloroform are freed from traces of moisture, alcohol, and hydrobromic acid, the longer is the formation of the crystals delayed. But even with the most carefully purified reagents I have never failed to obtain them sooner or later. Several samples prepared independently were filtered, washed with chloroform containing some bromine, and rapidly dried. The total bromine was estimated by Carius' method. The analysis gave the following results:

	Calculated for $C_8H_9ClN_4O_2.HBr.Br_5$.	Found. I.	II.	III.	IV.
Total bromine	67.66	65.98	....	66.57	....
Perbromine	56.38	55.25	55.02	55.42	55.00

The results of analysis show conclusively that we have here a perbromide of a hydrobromide. To confirm this, I have prepared the same compound by passing hydrobromic acid gas into a solution of chlorocaffeine and bromine in chloroform. The perbromide, which separated as a heavy amorphous sediment, gave these figures:

Total bromine	67.04
Perbromine	55.87

Whence comes the hydrobromic acid? Some of it at least is probably produced by the action of bromine upon traces of moisture present in the reagents. It is not improbable that some hydrobromic acid results from the substituting action of bromine upon chloroform, a reaction which is extremely slow when the reagents are pure, but may be induced or facilitated by the presence of foreign bodies, like chlorocaffeine in this case. Then again, a small portion of chlorocaffeine is probably decomposed, in some way, by bromine with the production of hydrobromic acid; and this, as soon as formed, unites with the unattacked chlorocaffeine and forms the perbromide. This would

explain why, even when pure reagents are employed, the formation of crystals begins very soon after the addition of bromine, provided it be added in large excess.

The perbromide, when crystalline, consists of dark-red short thick prisms. It melts at 151° C. It is decomposed by water, alcohol, ethyl acetate, giving a residue of pure chlorocaffeine. It is insoluble in chloroform. Ether removes only four-fifths of the "exterior" bromide, and gives a lower perbromide. Exposed to air it loses bromine quite readily, and if the exposure be prolonged, it loses all its bromine. Gentle heating greatly hastens the liberation of bromine.

Chlorocaffeine Hydrobromide Monobromide, $C_8H_9ClN_4O_2.HBr.Br$.—When the pentabromide of chlorocaffeine, finely powdered, is digested with anhydrous ether for several days, it gives up four-fifths of its "exterior" bromine. The reaction is slow towards the end and care must be taken to replace the ether with fresh portions of the solvent. The yellow residue is filtered off, washed with ether and rapidly dried. Several samples were analyzed with the following results:

	Calculated for $C_8H_9ClN_4O_2.HBr.Br$.	Found. I.	II.	III.
Total bromine	41.08	42.34	....	....
Perbromine	20.54	22.11	20.89	20.04

It is a yellow amorphous powder, of a darker shade than the corresponding derivative of bromocaffeine. It melts at 189° C., being previously decomposed into chlorocaffeine and bromine. It resembles the pentabromide in most of its properties, but seems to be somewhat more stable toward methyl and ethyl alcohol.

Chlorocaffeine Hydrochloride Pentabromide, $C_8H_9ClN_4O_2.HCl.Br_5$.—Chlorocaffeine is dissolved in dry chloroform containing bromine free from hydrobromic acid. A slow stream of dry hydrochloric acid gas is now passed into the solution. Beautiful well defined crystals soon separate. These are filtered, washed with chloroform containing bromine, and rapidly dried. Several samples gave the following results upon analysis:

	Calculated for $C_8H_9ClN_4O_2.HCl.Br_5$.	Found. I.	II.	III.
Br	60.17	58.88	57.62	58.50
HCl	5.48	5.61	....	....

The crystals, small prisms, are of a red to a scarlet-red color. The perbromide melts at 153° C. It is decomposed by water, alcohol, and ethyl acetate in about the same degree as the perbromide of the hydrobromide. On exposure to air, or on gentle heating, it does not seem to lose bromine any faster than the perbromide of the chlorocaffeine hydrobromide.

V. PERHALIDES OF BROMOCAFFEINE.

Bromocaffeine, like the chloro compound, is capable of forming salts and perhalides, provided the proper conditions are observed. In general, the salts are even more stable than those obtained from chlorocaffeine; this is also true, in general terms, of the perhalides.

Bromocaffeine[1] *Hydriodide*, $C_8H_9BrN_4O_2.HI$.—Prepared and analyzed like the corresponding salt of chlorocaffeine, it furnished these figures:

	Calculated for $C_8H_9BrN_4O_2.HI$.	Found. I.	II.	III.
HI	31.83	31.49	32.18	32.52

Kept over potassium hydroxide for two days it showed no loss of hydriodic acid.

Bromocaffeine Hydrobromide, $C_8H_9BrN_4O_2.HBr$.—This salt has to be washed with chloroform saturated with hydrobromic acid, for otherwise it dissociates and gives upon analysis low results:

	Calculated for $C_8H_9BrN_4O_2.HBr$.	Found. I.	II.	III.
HBr	22.89	21.22	19.00	23.50

The salt is tolerably stable when protected from moisture.

Bromocaffeine Hydrochloride, $C_8H_9BrN_4O_2.HCl$.—Prepared in the same manner as the other salts, it furnished the following results:

	Calculated for $C_8H_9BrN_4O_2.HCl$.	Found. I.	II.
HCl	11.77	11.79	11.43

This salt is far more stable than the hydrochloride of chlorocaffeine. Left over potassium hydroxide for twenty hours, it lost only 0.70 per cent. of hydrochloric acid.

Bromocaffeine Hydriodide Pentiodide, $C_8H_9BrN_4O_2.HI.I_5$.—This periodide has been prepared similarly to the analogous

[1] Prepared according to E. Fisher's method, *Ann. Chem.* (Liebig), 215, 264.

periodide of chlorocaffeine. Washed with chloroform, dried and analyzed, it gave the following results, as obtained upon separate samples:

	Calculated for $C_8H_9BrN_4O_2.HI.I_5$.	Found. I.	II.	III.
Total iodine	74.32	72.86	....	....
Periodine	61.22	60.52	60.22	61.27

It is a dull-black amorphous powder, melting at 183° C. It is decomposed by water, alcohol, ether, and ethyl acetate, but slower than the analogous periodide of chlorocaffeine. It is insoluble in chloroform. The sample that furnished analysis I. was boiled for some time with chloroform, and still gave upon titration with sodium thiosulphate 60.39 per cent. of iodine. It loses iodine very slowly on exposure, and even on warming, the liberation of iodine is slow.

Bromocaffeine Hydrobromide Pentiodide, $C_8H_9BrN_4O_2.HBr.I_5$. —This periodide forms very slowly, and the product, as first obtained, must be redigested in fresh solutions of iodine in chloroform, in order to insure a uniform and constant sample. When all the salt has been thus converted into the pentiodide, further digestion with iodine does not give any higher periodide; and when the pentiodide is washed with large quantities of pure chloroform, it loses none of its "exterior" iodine. Several samples were analyzed with the following results:

	Calculated for $C_8H_9BrN_4O_2.HBr.I_5$.	Found. I.	II.	III.
I	64.12	65.40	63.88	64.53
HBr	8.12	....	8.42	....

This periodide is amorphous, of a dark-brown color, and melts at 160° C. It is decomposed by the different reagents like the similar periodide of chlorocaffeine. Unlike the latter, it loses iodine only very slowly on exposure, but quite rapidly when warmed. In this respect, then, it is a more stable compound than its analogue of chlorocaffeine.

Bromocaffeine Hydrochloride Tetraiodide, $C_8H_9BrN_4O_2.HCl.I_4$. —Just as the hydrochloride salt of bromocaffeine is more stable than the hydrochloride of chlorocaffeine, so is the periodide of the former easier obtained in pure state than that of the latter. When hydrochloric acid gas is passed into a solution of bromo-

caffeine and iodine in chloroform, the periodide comes down at once pure, either in brown or dark-blue crystals, depending upon the rate with which the hydrochloric acid is passed into the solution. Samples were washed with chloroform containing hydrochloric acid, dried and analyzed with the following results:

	Calculated for $C_8H_9HBrN_4O_2.HCl.I_4$.	Found. I.	II.	III.
I	62.06	61.50	60.53	61.14
HCl	4.46	4.27	....	....

Bromocaffeine, then, agrees with chlorocaffeine in that respect that they both form *tetraiodides* of their respective hydrochlorides. The periodide of bromocaffeine hydrochloride is much less stable than the periodide of the hydrobromide, and in this respect bromocaffeine differs from chlorocaffeine, for in the latter the gradation of the stability is in the reverse order. This periodide consists of well-defined brown or dark-blue crystals, melting at 136° C. It is readily decomposed by the various reagents. Exposed to air, it loses nearly all its iodine in a comparatively short time, and still more rapidly when warmed.

Bromocaffeine Hydrobromide Pentabromide, $C_8H_9BrN_4O_2.HBr.Br_5$.—All that has been said about the formation of the perbromide of chlorocaffeine applies equally well in the case of bromocaffeine. A solution of the latter in chloroform containing bromine begins to deposit long slender crystals within five to six hours, and the crop gradually increases as the solution is allowed to stand. Even when the reagents employed are carefully freed from traces of moisture and hydrobromic acid, the formation of the perbromide still takes place, being more rapid as the amount of bromine added is increased. The perbromide, thus obtained, is entirely identical with the one which is formed when dry hydrobromic acid gas is passed into a solution of bromocaffeine and bromine in chloroform, except that in the latter case the product is amorphous. All that has been said about the possible sources of the hydrobromic acid in the case of the perbromide of chlorocaffeine, must apply fully as well to the perbromide of bromocaffeine. Uufortunately, neither of the two halogen substitution products of caffeine are soluble in carbon tetrachloride, and therefore the latter could not be used instead of

chloroform. The total bromine was found by subtracting from the total silver bromide, as obtained by Carius' method, that amount of it which corresponds to the bromine in bromocaffeine proper. The results of the analysis of several samples are as follows:

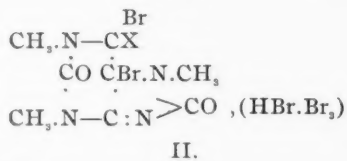
	Calculated for $C_8H_9BrN_4O_2.HBr.Br_8$.	Found. I.	II.	III.	IV.	V.
Total bromine.....	63.68	64.17	....	64.31	....	64.53
Perbromine	53.05	54.15	53.23	53.40	53.25	53.65

Analyses I, II, III and IV are upon samples prepared without the addition of hydrobromic acid, while Analysis V is upon a sample obtained with addition of the acid.

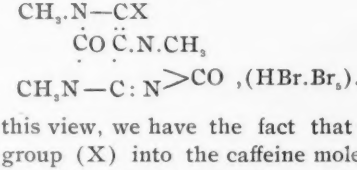
This perbromide consists of short prisms of a dark orange-red color, melting at 156° C. It resembles in general behavior the analogous perbromide of chlorocaffeine. It is decomposed by the various reagents, and on exposure loses all its bromine. When treated with ether it, too, forms the lower perbromide.

It may be said, that whatever the case be with pure caffeine itself, the perbromides of the halogen substitution derivatives of the base may after all have two bromine atoms linked to the unsaturated carbon atoms, and only the three remaining bromine atoms form the true perbromide. That is, the constitution of the perbromides should be represented by Formula I, and not by II.

I.



II.



In favor of this view, we have the fact that the introduction of a negative group (X) into the caffeine molecule favors the formation of such additive products. Thus, E. Fisher[1] has found

[1] *Ann. Chem.* (Liebig), **215**, 272.

that hydroxycaffeine readily unites with bromine, and the resulting additive product has not unlikely this composition : $C_8H_9(OH)N_4O_2.Br_2$. But against this view we have (1) that no such dibromo-additive compounds of either chloro or bromocaffeine has ever been isolated; (2) that even iodine makes the penta-perhalides, and not the tri-perhalides, as we should otherwise expect, and (3) that the formation of the perhalides of bromo and chlorocaffeine takes place only in presence of some halogen acid.

Bromocaffeine Hydrobromide Monobromide, $C_8H_9BrN_4O_2HBr.Br$.—This is formed when the higher perbromide is treated with anhydrous ether until fresh portions of the latter are no longer colored by the perbromine. Washed with ether and dried, several independent samples were analyzed with the following results :

	Calculated for $C_8H_9BrN_4O_2.HBr.Br_2$.	Found. I.	II.	III.
Total bromine	36.86	37.35	....	....
Perbromine	18.43	18.68	20.39	20.04

This perbromide is of a lighter yellow color than the corresponding perbromide of chlorocaffeine ; in all other respects the two compounds apparently agree. It melts at 206° C., suffering, previously to melting, decomposition into bromocaffeine, hydrobromic acid, and bromine.

Bromocaffeine Hydrochloride Pentabromide, $C_8H_9BrN_4O_2.HCl.Br_5$.—Bromocaffeine is dissolved in chloroform, bromine free from hydrobromic acid is added, and a slow stream of hydrochloric acid gas is now passed into the mixture. The separation of the perbromide begins to take place at once, in the form of deep-red needle-like crystals. Samples thus prepared were analyzed with the following results :

	Calculated for $C_8H_9BrN_4O_2.HCl.Br_5$.	Found. I.	II.
Br	56.40	55.25	55.18
HCl	5.13	5.02	....

This perbromide resembles very closely the perbromide of the hydrobromide, but it seems to give off bromine more readily than the latter. It melts at 157° C. It is decomposed by the various reagents, and gives pure bromocaffeine.

VI. SUMMARY.

The results described in the preceding pages are presented in a condensed form in the subjoined table. In general terms, the perhalides, as given in the table, decrease in stability as we read from left to right. For example, of the periodides of the hydriodides, that of caffeine is the most stable, next comes that of bromocaffeine, and this is followed by the one of chlorocaffeine. The same is true of the periodides and perbromides of the other salts. While the line is quite sharp between the perhalides of caffeine and those of bromocaffeine, it is not so between the perhalides of the latter and those of chlorocaffeine. We can speak only in general terms of a difference in stability between the perhalides of the two halogen caffeines, respectively. Thus, we notice such a difference in stability between the periodides of the two hydrobromides, and also between the perbromides of the two hydrochlorides respectively. The gradation in stability among the periodides of one and the same class is usually, but not always, regular. In all three cases, however, the periodides of the hydriodides are far more stable than those of the other salts. If *a*, *b*, and *c* should represent different degrees of stability, decreasing in alphabetical order, then the *relative* stability of the members of each class of the perhalides is as is given in the table. It must be understood that the term *stability* is used here in its broad and general sense, such as the behavior of the compounds towards different solvents, and on exposure to air. The comparison is made between the perhalides of each class, and periodides, as well as the perbromides of each of the three bases (caffeine, bromocaffeine, and chlorocaffeine) form separate classes for comparison. When two perhalides of the same salt exist, only the higher one is taken into account.

There appears to be a regular lowering in the melting-points of the periodides of each class, it being the highest in the hydriodides and the lowest in the hydrochlorides. It is a curious coincidence that the melting-points of the analogous periodides of chlorocaffeine and bromocaffeine are so near alike, while the pure halogen caffeines themselves melt at 188° C. and 206° C., respectively. The perbromides do not show such a regular gradation. There is a difference in stability of the periodides of each class, corresponding to the lowering of the

	Acid combined with base.	Caffeine. Perhalides.	Stability.	M. P.	Bromocaffeine. Perhalide.	Stability.	M. P.	Chlorocaffeine. Perhalide.	Stability.	M. P.
Periodides.	HI.	$C_8H_{10}N_4O_2.HI.I_2$		171°						
	HI.	$C_8H_{10}N_4O_2.HI.I_4$	*a*	215°	$C_8H_9BrN_4O_2.HI.I_4$	*a*	183°	$C_8H_9ClN_4O_2.HI.I_5$	*a*	185°
	HBr.	$C_8H_{10}N_4O_2.HBr.I_3$	*b*	183°	$C_8H_9BrN_4O_2.HBr.I_5$	*b*	160°	$C_8H_9ClN_4O_2.HBr.I_5$	*c*	169°
	HCl.	$C_8H_{10}N_4O_2.HCl.I_2$	*c*	165°	$C_8H_9BrN_4O_2.HCl.I_4$	*c*	183°	$C_8H_9ClN_4O_2.HCl.I_4$	*b*	137°
Perbromides.	HBr.	$C_8H_{10}N_4O_2.HBr.Br_2$		170°	$C_8H_9BrN_4O_2.HBr.Br.$		206°	$C_8H_9ClN_4O_2.HBr.Br$		189°
	HBr.	$C_8H_{10}N_4O_2.HBr.Br_4$	*a*	170°	$C_8H_9BrN_4O_2.HBr.Br_5$	*a*	156°	$C_8H_9ClN_4O_2.HBr.Br_5$	*a*	151°
	HCl.	$C_8N_{10}N_4O_2.HCl.Br_4$	*b*	149°	$C_8H_9BrN_4O_2.HCl.Br_5$	*b*	157°	$C_8H_9ClN_4O_2,HCl.Br_5$	*b*	153°

melting-points, this being true of caffeine and bromocaffeine, where the periodide of the hydrobromide is less stable than the hydrochloride. There is a uniformity in composition between the periodides on one hand and the corresponding perbromides on the other, in each of the three bases. Thus, in caffeine it is always the tetrahalide compound that is more easily formed, and in chlorocaffeine and bromocaffeine it is the pentahalide. It will be noticed that all three hydrochlorides carry less iodine in the periodides than the salts of the other two halogen acids.

It is difficult to draw very general conclusions from the study of perhalides of only one base, but so far as they go, the results presented in the preceding pages justify in a certain degree the following conclusions:

(1) Organic bases are capable of forming periodides not only of their hydriodide salts, but also of the hydrobromides and of the hydrochlorides. The stability of the resulting periodide will be governed, all other conditions being equal, by the nature of the halogen through which the "periodine" is linked to the nitrogen, decreasing as the volatility of the halogen increases.

(2) When a base forms periodides, it is also capable of forming perbromides, which probably possess an analogous composition and constitution.

(3) If two nearly related compounds form under similar conditions periodides (or perbromides) of different degrees, then the periodide (or perbromide) containing the highest number of "perhalogen" atoms is not necessarily the more stable of the two. Compare, for instance, the tetraiodide and tetrabromide of caffeine with the pentiodide and pentabromide of bromocaffeine.

(4) The number of iodine atoms which a base takes up in the formation of a periodide is in no way an index of the basal power of the base. Caffeine, for instance, is a very weak base, yet it forms higher periodides than the comparatively stronger bases of morphine, strychnine, atropine, etc. Again, chlorocaffeine and bromocaffeine, although far weaker than caffeine itself, forms higher periodides than the latter.

In conclusion, I wish to express my thanks to Mr. J. A. Keating and Mr. W. J. O'Brien, who have kindly helped me in this work.

ANN ARBOR, MICHIGAN.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 17.]

DETERMINATION OF THE HEAT OF BROMINATION IN OILS.[1]

BY H. W. WILEY.

Received January 3, 1896.

THE qualitative value of the degree of heat produced in mixing oils with sulphuric acid, is pointed out in Bulletin No. 13, Part IV, pages 475 *et seq*. In that bulletin a great number of examples are given, showing the different behavior of different fats and oils when treated according to the method first proposed by Maumené with sulphuric acid under standard conditions. It is evident that in a process of this kind the actual rise of temperature observed is dependent upon many varying conditions, such as the initial temperature, strength of sulphuric acid, relative proportions of sulphuric acid and oil employed, perfectness of insulation and other data depending on the analytical system itself. The data obtained under standard conditions, however, are extremely valuable in discriminating between fats of different characters. For instance, the rise of temperature produced by a given weight of butter fat is only about one-fourth of that produced by an equal weight of cotton oil under the same conditions. In the bulletin mentioned above, formulas are also given whereby some quantitative idea may be obtained of the relative proportions of the two constituents in a mixed oil. The fact that the natural glycerides contain unsaturated radicals capable of combining with the halogens has long been recognized, and Hübl, as is well known, has based a quantitative method of great value upon the ability of glycerides to absorb iodine. Chlorine and bromine are also absorbed with equal or greater avidity, and attempts have been made to establish quantitative methods in which these halogens take the place of iodine in the Hübl process.

Hehner and Mitchell[2] propose an innovation upon the general principles of the Hübl method in which the degree of chemical action is not measured by the residue of the halogen left unabsorbed, but by the degree of heat produced by the chemical reaction which takes place. They have not made any attempt

[1] Read at the Cleveland Meeting, December 31, 1895.

[2] Analyst, 20, 146.

to determine the total quantity of heat by calorimetric measurement, but simply estimate the total rise of temperature produced by the reaction. This method I have subjected to a thorough analytical test, and am convinced that it has great value in

analytical operations. On account of the difficulty of executing the method as described by the authors, I have made a number of changes therein which render it not only more accurate, but, especially, more easy of application. The difficulty of handling liquid bromine in quantities of one cc. is evident to every

analyst. It is almost impossible to measure and deliver exactly this quantity of liquid bromine into the tube in which the reaction takes place. I have therefore made use of the bromine previously dissolved in chloroform or carbon tetrachloride. I find that one part by volume of bromine in four parts by volume of chloroform makes a solution which is easily kept and easily measured. To avoid any disturbing action of the bromine upon the chloroform, due to the generation of hydrobromic acid, the solution should be kept shielded from the light and only small quantities, such as may be used during the day, made up at a time. Another convenient modification has been introduced in dissolving the fats or oils in chloroform or carbon tetrachloride before beginning the analytical operations. By this means triplicate determinations, or a greater number may be made on the same sample without the trouble and annoyance of weighing each one. Ten grams of the oil or fat are dissolved in chloroform and the volume made up to fifty cc. With this volume nine determinations can easily be made, and it is recommended that at least four be made with every sample.

The apparatus employed is shown in the illustration. The tube holding the reagent and thermometer is about forty centimeters in length and one and a half in internal diameter. It is conveniently held in a drying jar, into which it fits air-tight by means of a rubber stopper. In order to secure the insulation of the inner tube, the air is withdrawn from the drying cylinder through the side tubulure. The solution of bromine and chloroform is placed in a heavy Erlenmeyer flask with a side tubulure near the top, to which is attached a rubber bulb. The flask carries a pipette held in place by a stopper, which by gentle pressure is made air-tight. The thermometer used is graduated in fifths of degrees and is easily read to tenths by means of a small magnifying glass.

The operation should be conducted in a room which is kept at as nearly as possible constant temperature during the progress of the work.

The solutions having all been prepared, they are placed upon the table with the apparatus and the whole system is allowed to stand until a constant temperature through all parts is reached.

Five cc. of the solution of the fat or oil are placed in the inner tube by means of a pipette, with care to prevent the solution coming in contact with the walls of the tube. The thermometer having been inserted, the bromine solution is forced into the pipette by compressing the rubber bulb with the left hand until the liquid has passed the mark on the stem of the pipette. The top of the pipette is now closed by the forefinger of the right hand, the pressure on the rubber bulb released, the stopper in the Erlenmeyer flask loosened and the bromine in the pipette allowed to flow out until the mark is reached. The bromine solution is transferred to the observation tube and allowed to flow directly into the solution of the fat. It is not important, in this case, to prevent the liquid from touching the sides of the tube as it enters. As soon as the pipette is empty it is withdrawn, replaced in the Erlenmeyer flask and the thermometer at once observed by means of the magnifying glass. The bromination of the fat is practically instantaneous and the mercury in the thermometer will reach its maximum height in about a minute after the pipette delivering the bromine solution is withdrawn. The whole operation of determining the heat of bromination after all the preparations are made can be accomplished within two minutes. When the mercurial column in the thermometer begins to descend, air is admitted into the outer cylinder through the stop-cock shown, the tube containing the residue of the reaction is withdrawn by loosening the rubber stopper and its contents emptied. By holding the tube with the mouth down the residual bromine vapor soon escapes and the tube may be cleaned by simply wiping it with a long test-tube cleaner, or may be used again without cleaning afteral lowing it to stand for half an hour mouth down. Any traces of brominated oil which remain upon the sides of the tube do not unfit it for subsequent use, unless thick enough to obscure the reading of the temperature. By allowing the air thus to reenter the jacket space the thermometer is soon restored to normal, and a second determination may be made within half an hour. In this way two determinations an hour can be made with the same system.

In regard to the relation which the rise of temperature, due to

bromination, has to the iodine absorption number of a fat, it is stated by Hehner and Mitchell that it is represented by the factor 5.5. It is evident, however, that this factor must be determined separately for every system of apparatus and every solvent employed. Naturally it would be different from the number stated when determined in the manner indicted above. Each analytical system, therefore, must be separately standardized, and the factor thus obtained can be used with considerable certainty for calculating the number representing the iodine absorption.

It may be mentioned that it is important not to stir or churn the mixture of the oil and bromine further than is secured by the introduction of the bromine solution itself. By a vigorous churning of the mixture, throwing the warm liquid against the cold side of the containing tube, I found it possible to reduce the rise of temperature in one instance from 19° to less than 15°. It is evident that much more accurate results could be obtained in all cases by a careful calorimetric measurement of the heat produced by the reaction. For strictly scientific purposes, this is the only rational method of procedure, but the desired end will be served equally well by carefully conducting the process in some such way as indicated above and determining for each system of apparatus employed the factor for calculating the iodine number.

Experience has shown that carbon tetrachloride, by reason of its higher boiling-point and stability, is a more convenient solvent in the preparation of the reagents than chloroform. The rise of temperature obtained, however, with solutions in carbon tetrachloride, is slightly less than in chloroform. This is not due to a higher specific heat of the carbon tetrachloride, since at 30° the specific heats of the solvents are 0.207 and 0.233 for carbon tetrachloride and chloroform respectively. Either the action of the bromine is more vigorous in the chloroform solution or else the heat due to the bromination of the chloroform and the production of hydrobromic acid is sufficient to account for the difference. In other words, we have here to deal not only with the heat of bromination of the oil, but also with that due to the formation of $CBrCl_3$ and of hydrobromic acid. This is an addi-

tional reason for preferring carbon tetrachloride as a solvent.

This action is indicated by the following data: One part of bromine and four of chloroform were placed in separate contiguous vessels, in a room subject only to slow changes of temperature, and left at rest for nineteen hours. The temperature of the two liquids at the expiration of this time was exactly 12°. On placing the thermometer in the bromine and pouring the chloroform upon it there was at first a depression of the temperature amounting to seven-tenths of a degree. In a few seconds the temperature began to rise, and at the end of three minutes it had reached 13.3°, showing a rise of over one degree above that of the original solutions.

In the following table the data representing the means of several observations in each instance are given, showing the results of the determination of the heat of bromination of four oils dissolved in the one instance in chloroform and the other in carbon tetrachloride:

Name of oil.	Solvents.	Initial temperature.	Final temperature.	Rise of temperature.
Olive oil	Chloroform	22.7°	42.2°	19.5°
Olive oil	Carbon tetrachloride	15.1	33.3	18.2
Calycanthus seed oil	Chloroform	17.2	45.9	28.7
Calycanthus seed oil	Carbon tetrachloride	19.3	47.0	27.7
Salad oil (cotton seed?)	Chloroform	17.9	43.7	25.8
Salad oil (cotton seed?)	Carbon tetrachloride	19.8	44.7	24.9
Sunflower seed oil	Chloroform	15.0	43.4	28.4
Sunflower seed oil	Carbon tetrachloride	14.0	41.6	27.6

My thanks are due to Mr. E. E. Ewell for assistance in the analytical work.

DISCUSSION.

Dr. C. B. Dudley: The detection of adulterations in commercial oils is a subject that has given us an immense amount of study in the laboratory at Altoona. The commercial results may be easily imagined when it is known that at one time during the past eighteen years lard oil was worth $1.10 a gallon, and cottonseed oil fifty cents a gallon, and that it was no uncommon practice to put into a gallon of lard oil as high as twenty-five per cent. of cottonseed oil. I should state that lard oil is used in making burning oil for hand lanterns and is commonly called signal oil. On this oil depends largely the safety of the running of

trains. Cottonseed oil being, as you all know, a semi-drying oil, and does not burn well, hence the seriousness of adulteration may be readily understood. Signal oil mixed with cottonseed oil will go out in from six to eight hours after it is lighted, at least after the first two or three times burning of a wick. The switches must be lighted fourteen hours continuously to insure safety, and the hand lanterns for signalling must be reliable. No small amount of the work done at Altoona has been done in connection with adulterations in oils. We have kept pace with every modification that would enable us to detect adulteration, and have found Maumené's test of very great value, because of its simplicity, its rapidity of application, and the constancy of the results obtained.

There are two serious defects, however, in all the tests that I have ever seen proposed for detecting adulterations in oils. These are: First, none of the proposed methods are based on any characteristic reactions of any given oil so that although we may be able to say that a sample of oil submitted to us is not pure, we are unable to say what other oil it is adulterated with. The second defect is that owing to this lack of characteristic reactions and to the peculiarities of the proposed method, mixtures of various oils can be made, which mixtures will give the same results under the tests as a pure sample of another oil. For example, it is quite easy to make such a mixture of olive and cottonseed oils that the rise in temperature obtained by Maumené's test will be the same as is characteristic of pure lard oil. And the same may be said of the iodine test, etc. So far as our knowledge goes we still lack a means of identifying the characteristic oil that may be present as an adulterant in another, and also we still lack an absolute means of saying positively that a sample of an oil is not a pure one.

SÄRNSTRÖM'S METHOD OF DETERMINING MANGANESE IN IRON ORES.

By C. T. Mixer and H. W. DuBois.

Received February 25, 1896.

ABOUT a year ago we had occasion to use a volumetric method which would allow the determination of manganese in iron ores ranging in amounts up to fifteen per cent. and give results in half an hour which would check with gravimetric determinations within two-tenths per cent. for ores as high as fifteen per cent., and within a few hundredths of a per cent. for ores under one per cent.

We found in use in a neighboring laboratory a method which was generally known as the "Swedish Method." This method was found to fulfil the above conditions, and seems to have sufficient merit to be more widely known.

The first suggestion upon which the method is based was made by Guyard,[1] although his method of operating it did not give very satisfactory results.

The first description of the method in its present practicable form, was made by C. G. Särnström, in the Jernkontorets Annaler, (Sweden), 1881, p. 401.[2]

The principle upon which this method depends, is the reaction which takes place when a manganese compound higher in oxygen than the manganous state, is dissolved in hydrochloric acid, forming a higher chloride, which is readily shown by the dark colored solution. When the solution is boiled, it rapidly decolorizes, being completely converted into manganous chloride, not easily oxidized by the air while in the acid solution.

In neutral or alkaline solutions the manganous compound has a slight tendency to oxidize in contact with the air, but we have never detected any appreciable oxidation under the conditions which we follow.

The separation of the iron and the manganese is effected in

[1] Guyard: *Chem. News*, **8**, 292; the following references relate to the subsequent modifications of the method; Habich: *Ztschr. anal. Chem.*, **3**, 474; Winkler: *Ztschr. anal. Chem.*, **3**, 423. Morawski und Stingl: *J. prakt. Chem.* (N. F.), **18**, 96; Volhard: *Ann. Chem.* (Liebig), **198**, 318.

[2] Also published in Berg und Hüttenm. *Zeitung*, **40**, 425. A review of the original article appears in the *Ztschr. anal. Chem.*, **22**, 84. We are indebted to Mr. Hugo Carlsson, Chief Chemist of the Johnson Works of Lorain, Ohio, for calling our attention to Särnström's original publication and for furnishing us a translation of the same.

such a way that the iron is precipitated as hydroxide and the manganese left in the manganous condition in solution. Sodium carbonate is used to precipitate the iron as hydroxide and no trouble is experienced in the precipitation of the manganese as a carbonate, provided that only a very slight excess is employed beyond that necessary to completely precipitate the iron.. It is advisable to add the sodium carbonate in the form of a solution, towards the completion of the precipitation of the iron, to avoid such an excess.

Särnström employs sodium bicarbonate, which has the advantage that a greater amount of carbon dioxide is generated, preventing subsequent oxidation of the manganous salt by the oxygen in the air. Manganese bicarbonate is formed, which is readily soluble in the solution containing carbon dioxide.

It is always desirable to test the sodium carbonate or bicarbonate for organic matter.

The results given below show the necessity of avoiding an excess of sodium carbonate (the same is true of the bicarbonate) in the precipitation of the iron. Aliquot portions of a solution of manganese containing 3.14 per cent. manganese gravimetrically determined, gave only 2.61 per cent. when treated with such an excess. Another one giving 8.69 per cent. under the proper conditions of this method, when treated with an excess of sodium carbonate, gave 5.38 per cent.

After the precipitation of the iron in the hot solution, the manganese, being in the manganous state, is oxidized by potassium permanganate, according to the following formula,

$$3MnO + 2KMnO_4 + H_2O = 2KOH + 5MnO_2,$$

which is the same reaction which takes place in Volhard's method. As the titration takes place directly, without filtering, the precipitate of ferric hydroxide is an advantage, especially in low manganese ores, as it serves to collect the fine precipitate of manganese dioxide and causes it to settle more rapidly.

In ores very low in iron, it is desirable to add ferric chloride in order to obtain the requisite amount of the iron precipitate.

The Method.—Weigh half a gram ore into a No. o beaker, add fifteen cc. of hydrochloric acid 1.1 sp. gr., and boil until

the residue is clear. If necessary fuse the residue with sodium carbonate. Add a few drops of nitric acid to oxidize any ferrous iron or organic matter. In magnetic ores more of course will be necessary. It is well to test for ferrous iron. Evaporate a short time to expel any nitrous acid that may have been formed. It is advisable to have a good amount of free hydrochloric acid present to generate carbon dioxide in the precipitation with sodium carbonate. The solution is then washed into a No. 3 beaker or flask, which is then filled about two-thirds full with boiling, distilled water and solid sodium carbonate or bicarbonate added until the iron is completely precipitated, which is readily indicated by the characteristic spongy appearance of the precipitated ferric hydroxide. A solution of the salt is preferable for the final precipitation in order to avoid an excess.

The solution should be about 80° C. when it is titrated[1] with potassium permanganate directly, without filtering, and with intervals of vigorous stirring and settling of the iron and manganese precipitates, until the supernatant liquid shows a permanent faint pink color. The first appearance of the pink color must not be taken as an indication that the oxidation is complete, as gentle heating and vigorous stirring will allow more potassium permanganate to be added before the permanent pink appears.[2]

Multiplying the burette reading by two represents the equivalent for one gram, and this multiplied by the permanganate value in manganese, which is the iron value multiplied by 0.2946, gives the percentage of manganese.

In case of over-titration, it is practicable to titrate back with a carefully standardized solution of manganous chloride, which is prepared by evaporating fifteen cc. potassium permanganate down to three or four cc., adding a few drops of hydrochloric acid and boiling as long as chlorine comes off. The solution should be neutralized with sodium carbonate and diluted to ten cc., when one cc. is equal to one cc. of potassium permanganate.

Särnström states that the method is reliable for high manga-

[1] Which should be done immediately after the neutralization, in order to avoid any opportunity for oxidation.

[2] This is a very important point not only in relation to this method, but in all methods where potassium permanganate is used.

nese ores and ferro-manganese " where it is not necessary to determine the manganese closer than a few tenths of one per cent."

Our experience does not confirm this. The results average from one to two per cent. too low, so that we do not consider the method at all reliable for high percentages of manganese.

The following are some results which show this :

	Särnström. Per cent.	Gravimetric (Ford's) Per cent.
Illinois Ore	52.06 (1)	52.98
	51.91 (2)	....
	51.40 (3)	....
	51.78 (4)	...
	51.37 (5)	....
	51.37 (6)	....
No. 595	42.07	....
	42.35	44.3
	42.90	....
	42.60	....

In analyses from No. 1 to No. 4 sodium carbonate was used for the precipitation. To determine whether the employment of sodium bicarbonate would be advantageous, No. 6 was so treated while at the same time No. 5 was precipitated with sodium carbonate, yielding the same result. We have tried sodium bicarbonate with low manganese ores, but have never noticed any practical advantages, while theoretically, as we have pointed out above, there should be an advantage in the employment of sodium bicarbonate.

This discrepancy with high percentages of manganese may possibly be accounted for, by the fact that the large precipitate of manganese dioxide may act in a purely mechanical way in protecting the final amounts of the manganous chloride from being fully oxidized to dioxide by the potassium permanganate. It is to be noted in this connection that Volhard's method does not generally give reliable results with such high percentages of manganese.

The following are some results obtained by this and other methods :

	Särnström.	Volhard.	Gravimetric.
A. Magnetic	0.07	0.10	0.07
Specular	...	0.08[1]	...
B. Mixture of blue granular and red hematite.	0.30	0.31	0.29
	0.32	0.29	0.30
	0.28	...	...
C. Limonite	1.03	1.02	1.09
	1.05	1.05	...
D. Silicious ore	2.98	3.08	2.93
	3.07	3.07	...
Cary Empire	3.93	T. V. Church	3.94
	3.88	Illinois Steel Co	
Dexter No. 2	6.04	...	...
	6.02	6.02	6.01
	6.01	...	...
Davis ore	8.78	8.62	8.86
Newark ore	1.48	A. G. McKenna, Duquesne Steel Works,	(Ford's) 1.50
No. 57	5.39	5.39	...
No. 218	5.59	5.59	...

In the determination of small amounts of manganese this method presents an advantage over Volhard's method in giving a more distinct end reaction.

The method can be used for iron and steel determinations if the usual precautions are taken to oxidize the carbon. But it is not so well adopted to these on account of the impracticability of taking large amounts for analysis.

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ON VARIOUS MODIFICATIONS OF THE PEMBERTON VOLUMETRIC METHOD FOR DETERMINING PHOSPHORIC ACID IN COMMERCIAL FERTILIZERS.

BY F. P. VEITCH.

Received February 18, 1896.

IF an excuse is needed for adding to the already voluminous literature on the method as proposed by Pemberton[2] and modified by Kilgore, it is found[3] in the action taken by the Association of Official Agricultural Chemists at their last meeting. The method, as modified by Kilgore, gave almost uniformly excellent results on known solutions, in a two years trial in the hands of a number of analysts, and only failed to become

[1] This was so low as to necessitate filtering through asbestos in order to see end reaction by Volhard's method.

[2] This Journal, 15, 382.

[3] Bul. 43, Div. Chem. U. S. Dept. Agr., 104.

an official method because many of the members had not worked with it.

During the past fall the writer has used the Kilgore modification as a check in quite a number of gravimetric determinations with very satisfactory results. While this modification may be considered as accurate as the molybdate for this class of work, at least on low percentages and in careful hands, it was felt that if the exact time and temperature elements could be gotten rid of, there would be a saving of both time and care where a large number of determinations were to be made. With this end in view, it was determined to study the following points :

1. The method of filtering and washing.
2. The time of standing after adding the molybdate solution.
3. The use of tartaric acid to prevent the precipitation of molybdic acid.

With regard to the first point it was found desirable to use simply the paper and funnel, doing away with the use of pressure and filtering twenty at a time. To simplify washing the dilute nitric acid and three per cent. potassium nitrate were omitted from the washings.

As the filter paper and funnel have been used with pressure with satisfactory results, there seems to be no objection to the use without pressure, so to condense the work as much as possible, the subjects were studied in pairs, as follows :

A. The method of filtering and washing and the time of standing after adding the molybdate solution.

B. The method of filtering and washing, and the use of tartaric acid to prevent the precipitation of molybdic acid.

A. THE EFFECTS OF THE METHOD OF FILTERING AND WASHING AND THE TIME OF STANDING AFTER ADDING THE MOLYBDIC SOLUTION.

After some preliminary work, during which the volumetric method, as carried out at the New Jersey Station,[1] was tried and found to work very satisfactorily, it was determined to try the effect of standing for one half hour and for one hour at from 40°–50° C. It was thought best to allow some range of tempera-

[1] Bul. 43, Div. Chem. U. S. Dept. Agr., 92.

ture, as the care required to maintain a constant temperature is considerable.

The molybdate used was the official solution, to which ten cc. 1.42 sp. gr. nitric acid per cubic centimeter had been added. After standing the required length of time, the solutions were filtered off without pressure, the precipitates washed three times by decantation, allowing the precipitate to settle each time before decanting, the precipitates then transferred to the filters, the beakers washed out thoroughly and the precipitates washed until the wash water was neutral to litmus paper, which required from 200 cc. to 300 cc.; this latter amount has been found to free the precipitate from adhering acid in every instance. To feel sure that no appreciable amount of acid was retained in the filter, the washing was continued in a number of cases after no reaction was given with litmus paper, the washing received in clean beakers and titrated with the standard solutions. Table I gives the amount of acid removed by this extra washing as expressed in percentages of P_2O_5.

TABLE I.—THE AMOUNT OF ACIDITY EXPRESSED AS P_2O_5 RETAINED IN PRECIPITATES AFTER WASHINGS WERE NEUTRAL TO LITMUS PAPER.

Number.	Amount of washing until neutral to litmus paper.	Amount of washing after neutral to litmus paper.	Amount of acidity in last wash water, expressed as P_2O_5.	Per cent. P_2O_5 in precipitate on filter.	Remarks.
	cc.	cc.	Per cent.	Per cent.	
1	140	50	0.00	2.14	
2	135	"	0.01	2.81	
3	140	"	0.01	1.88	
4	200	"	0.04	1.48	Blue on filter hard to free from acid.
5	150	"	0.00	2.52	
6	225	75	0.05	9.68	
7	"	"	0.025	12.93	
8	"	"	0.025	6.46	
9	"	"	0.025	15.35	
10	"	"	0.000	15.28	
11	"	"	0.000	10.10	
12	"	"	0.000	17.09	
13	"	"	0.000	17.65	
14	"	"	0.025	22.10	
15	"	"	0.015	20.77	

Average..... 0.016 per cent.

These results show that when the washings become neutral to litmus paper, the precipitates are practically free from acid. It may be well to call attention to the fact that a first-class grade of filter paper should be used, otherwise the precipitate may run through the filter.

In Table II the results obtained when the solutions stood one-half and one hour and were then treated as above mentioned are compared with the gravimetric.

TABLE II.—COMPARISON OF TIME OF STANDING.

	Stood one-half hour at 40°–50°.					Stood one hour at 40°–50°.			
Number.	Washings.	Per cent. standing one-half hour.	Per cent. gravimetric.	Difference + or — from gravimetric.	Number.	Washings.	Per cent. stood one hour.	Per cent. gravimetric.	Difference + or — from gravimetric.
1	200	0.50	0.58	—0.07	1	200	1.84	1.75	+0.09
2	"	2.58	2.42	+0.16	2	"	1.96	1.79	+0.17
3	"	2.86	2.74	+0.12	3	"	2.38	2.38	0.00
4	"	2.06	2.17	—0.11	4	"	2.14	2.03	+0.11
5	"	2.10	2.17	—0.07	5	"	1.58	1.47	+0.10
6	"	5.00	5.06	—0.06	6	"	2.56	2.74	—0.18
7	"	4.41	4.56	—0.15	7	"	4.87	4.78	+0.09
8	"	3.06	3.08	—0.02	8	"	1.39	1.39	0.00
9	"	1.89	1.88	+0.01	9	"	2.08	2.07	+0.01
10	"	0.59	0.61	—0.02	10	"	2.88	3.06	—0.18
11	"	3.42	3.32	+0.10	11	"	2.40	2.54	—0.14
77	"	1.69	1.56	+0.12	12	"	3.43	3.25	+0.18
					13	"	3.18	3.33	—0.15
	Average difference.....			0.085	14	"	1.42	1.39	+0.03
	Difference of averages.			+ 0.0016	15	"	1.01	0.91	+0.10
						Average difference.....			0.102
						Difference of averages..			+0.015

From these results it appears that standing as long as one hour before filtering does not give results differing from the gravimetric more than the allowance for duplicates by that method. These results are not what was to have been expected from Kilgore's[1] experiments with various molybdates, as he found that both the official solution and that used by Pemberton gave deposits of

[1] Bul. 43, Div. Chem., U. S. Dept. Agr., 103.

molybdic acid in less than half an hour when heated to 60°. This difference is possibly explained by the fact that the ratio of nitric acid to the molybdic acid in solution was much greater than in his experiments, due to the precipitation of most of the molybdic acid by the phosphoric acid present.

B. THE EFFECT OF THE METHOD OF FILTERING AND WASHING AND THE USE OF TARTARIC ACID TO PREVENT THE PRECIPITATION OF MOLYBDIC ACID.

Jüpner's[1] experiments indicate that the precipitation of molybdic acid may be entirely prevented by the use of tartaric acid; also that the higher the temperature of precipitation the more tartaric acid required to keep the molybdic acid in solution.

Kilgore,[2] whose results are published since this work was done, comes to the conclusion that the use of citric acid for this same purpose possesses no advantage over the official molybdate solution, to which ten cc. of nitric acid per hundred has been added, and requires much longer time for the complete precipitation of the ammonium phosphomolybdate.

In the work given below the official molybdate solution plus ten cc. nitric acid and one gram tartaric acid per 100 cc. was used. A very little work soon proved that adding the molybdate to the phosphate solution at 30°, and allowing to stand one hour at the temperature of the laboratory, will not give satisfactory results, and standing one hour at 30°, gave very little better results, the ammonium phosphomolybdate remaining in solution and precipitating some time after running through the filter. Standing over night in the cold, however, gave excellent results, on low percentages, upon which alone it was tried. It was next determined to try the plan of allowing solutions to stand at 40°–50° for one hour and for two hours; the results, which are in most instances, comparable with those obtained by the gravimetric method, are given, with the results by the method of allowing to stand over night, in Table III.

[1] Abs. Expt. Record, 6, 610.
[2] This Journal, 17, 960.

TABLE III.—COMPARISON OF TIME OF STANDING, USING MOLYBDIC SOLUTION CONTAINING TARTARIC ACID.

Stood one hour at 40°–50°.					Stood two hours at 40°–50°.					Stood over night in the cold.				
Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or − from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or − from volumetric.	Number.	Washing.	Per cent. by molybdate containing tartaric acid.	Per cent. by volumetric.	Difference + or − from volumetric.
1	250	4.76	6.35 6.20	−1.51	1	275	1.40	1.33	+0.07	1	200	0.99	0.92	+0.07
2	"	2.54	2.38	+0.16	2	"	0.94	1.20	−0.26	2	"	2.14	2.16	−0.02
3	"	1.48	1.64	−0.16	3	"	0.65	0.50	+0.15	3	"	0.76	0.79	−0.03
4	"	2.41	2.57	−0.16	4	"	3.15	3.26	−0.11	4	"	1.35	1.32	+0.03
5	"	4.79	6.75 6.82	−2.00	5	"	2.77	2.85	+0.19	5	"	0.42	0.44	−0.02
6	"	1.81	2.28	−0.47	6	"	1.58	1.50	+0.08	6	"	1.70	1.65	+0.05
7	"	1.91	1.96	−0.05	7	"	2.20	2.08	+0.12	7	"	2.81	2.88	−0.07
8	"	2.22	2.06	+0.06	8	"	2.49	2.42	+0.07	8	"	1.12	1.12	0.00
9	"	0.72	0.69	+0.03	9	"	2.48	2.32	+0.16	9	"	1.56	1.49	+0.07
10	"	0.90	1.35 1.32	−0.44	10	"	2.28	2.40	−0.12	10	"	1.68	1.65	+0.03
					11	"	2.18	2.39	−0.19	11	"	1.18	1.10	+0.08
										12	200	2.52	2.55	+0.07

From these results it would appear that standing at 40°–50° for one hour is not to be relied on, at least for low percentages, the results in all cases being too low. Standing at 40°–50° for two hours, however, tends to give results slightly higher than those obtained by the volumetric method, while standing in the cold over night gives results practically identical with it.

This work of determining the temperature and time of standing that would probably give the best results, was done with low percentage solutions, as they were the most convenient at the time.

The figures so far obtained indicated that for further study with the official molybdate solution containing ten cc. of nitric acid extra, standing one-half hour at 40°–50°, was to be preferred, as standing for one hour tends to slightly high results.

It is believed, however, that standing for one hour will still give results comparable with results by the gravimetric method, but the precipitates require more washing, and longer time is required to complete the determinations.

For the further study of the use of tartaric acid, standing at 40°–50° for two hours, was selected.

For this final comparison of the various modifications solutions of fertilizers in which the phosphoric acid had been carefully determined gravimetrically by Mr. W. W. Skinner, were used. The samples cover practically all grades of commercial fertilizers, and have quite a range in percentage of phosphoric acid. The solutions and precipitates in both modifications were treated alike in all cases, except the time of standing.

TABLE IV.—COMPARISON OF VARIOUS MODIFICATIONS WITH THE GRAVIMETRIC.

Number.	One gram tartaric acid per 100 cc. molybdate two hours at 40°–50°.	Official molybdate + ten cc. HNO_3 per 100 cc. one-half hour at 40°–50°.	Gravimetric. (Skinner).	Volumetric.	Difference + or − from gravimetric. Titrated. Molybdate.	Difference + or − from gravimetric. Official molybdate + ten cc. HNO_3 per 100 cc.
1	9.73	9.68	9.75	....	−0.02	−0.07
2	15.65 15.42 (12.85)[1]	15.35	15.34	15.45	+0.16	−0.01
3	13.05 13.15	12.93	13.06	....	+0.04	−0.13
4	6.60 }[2] 6.68 }	6.48[2] 6.43[3]	6.30	....	+0.34	+0.16
5	13.35 10.00	13.23	13.35	....	0.00	0.07
6	9.95 (10.33)[1]	10.10 10.20	10.19	....	−0.21	−0.00
7	17.10 17.20	17.03 17.15	17.40	16.93	−0.25	−0.31
8	17.70 17.68	17.60 17.70	17.94	17.65	−0.25	−0.29
9	22.08 22.08	22.10	22.29	22.15	−0.21	−0.19
10	20.95	22.68 20.85	20.85	....	+0.10	−0.07
Average	14.617	14.541	14.647		0.156	0.141
		Difference of averages.....			−0.03	−0.10

In several instances where the modified methods gave decidedly lower results than the gravimetric method, the determinations were also made by the Kilgore modification, the results

[1] Omitted from averages.
[2] Fifteen cc. molybdate used.
[3] Ten cc. molybdate used.

agreeing in all cases with the results by the modified methods.

The results agree fairly well with the reported results by the Kilgore method, which averages slightly lower than the gravimetric results. The average difference by these modifications is 0.156 and 0.141 per cent., and the average of the plus and minus differences is 0.03 and 0.106 by the titrated molybdate and by the Kilgore molybdate respectively.

Only two results are noticeably higher than the gravimetric, and only one of these differs by more than two-tenths per cent. This seems to be due to the presence of a great excess of molybdate, as it will be noticed that when less molybdate was used the result was nearer the gravimetric. From the observation of quite a number of results, the writer believes that the amount of molybdate added should not be more than enough to precipitate one and a half times the phosphoric acid found to be present, otherwise the results are too high.

From the figures presented the following conclusions may be drawn :

1. The molybdate solution, to which nitric acid has been added, standing one-half hour at 40°–50°, gives results comparing very favorably with the gravimetric.

2. While the use of tartaric acid in the molybdate solution gives good results, it possesses no advantage and the extra time of standing makes it not so desirable.

The official molybdate plus ten cc. nitric acid per 100 cc., using the funnel and paper without pressure in filtering, and only water for washing is preferred by the writer to the usual way of carrying out the volumetric method ; this admits of a better distribution of the work, which makes in his hands a more rapid method where a large number of determinations are to be made.

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[Contributions from the Chemical Laboratory of the U. S. Department of Agriculture, No. 18.]

INDEX TO THE LITERATURE ON THE DETECTION AND ESTIMATION OF FUSEL OIL IN SPIRITS.

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Received September 20, 1895.

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THE OCCURRENCE OF TITANIUM.

By Charles E. Wait.

Received February 11, 1896.

IT is not my present purpose to repeat what has been already frequently published relative to the presence of titanium in minerals, typical rocks, meteorites, clays, soils blast furnace products, etc. I wish merely to call attention to the fact that some of the bodies with which we have much to do contain titanium, and that probably owing to the difficulties formerly

experienced in its estimation, it has been more frequently overlooked than is generally supposed.

In the recent examination of food materials, under the direction of the United States Department of Agriculture, I have had occasion to make analyses of the ashes of some plant materials, and this having led to further investigations, I was interested and surprised to find titanium present in every plant ash thus far examined.

This is in fact surprising, as it is stated by some writers[1] that "it does not appear to form part of the animal or vegetable kingdom."

The amount of titanic oxide found in the ash of some vegetable material is as follows:

	Per cent.
Oak wood	0.31
Apple and pear wood mixed	0.21
Apple	0.11
Cow peas	0.01
Cottonseed meal	0.02

From the above determinations we are reasonably safe in assuming that titanium is assimilated by plants. If this is true, it seems very strange that reference to this fact has not been made by recent writers upon agricultural chemical analysis, and upon the chemistry of vegetable life.

In fact, in consulting treatises on ash analysis with tables,[2] I do not find any mention whatever of the presence of titanium. If this is a fact, can it be true that it has escaped the attention of chemists for so long a time?

The examination of the ash of bituminous and anthracite coal shows the presence of titanic oxide. The results of some determinations are as follows:

	Per cent.
Jellico (Tenn.) bituminous coal	0.69
Coal Creek (Tenn.) bituminous coal	0.95
Pocahontas (Va.) bituminous coal	0.94
Middlesborough (Ky.) bituminous coal	0.83
Pennsylvania anthracite coal	2.58

[1] Roscoe & Schlorlemmer.
[2] Wolff.

With reference to the presence of titanic oxide in the ash of coal, it may be fairly assumed that partly owing to the infiltration of clay and earthy materials, it would be found there, but is it fair to assume that its presence is wholly accounted for in that way? If mention has been made of the presence of titanium in the ash of coal, it has thus far escaped my attention.

The method employed in the above determination is that of A. Weller,[1] which is based upon the fact that hydrogen peroxide, when added to a solution of titanium, produces a compound of an intensely yellow color. There are precautions necessary in the execution of this method which have already been pointed out.[2]

It will be my pleasure to report additional notes at an early day concerning the presence of titanium in the vegetable kingdom. Valuable service has been rendered in the above work by Messrs. J. O. LaBach and C. O. Hill.

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THE ESTIMATION OF PYRRHOTITE IN PYRITES ORES.

BY EDWIN F. CONE.

Received January 22, 1896.

SOME of the American pyrites ores contain the mineral pyrrhotite (Fe_7S_8) in varying proportions. In the manufacture of sulphuric acid from these ores it is found impossible to burn out at least the greater part, if not all, of the sulphur which is present as pyrrhotite. In the estimation of total sulphur in the sample of such an ore, of course the sulphur present as pyrrhotite is included. It is therefore necessary, in order to make a settlement with the company selling the ore and also in order to figure the yield of acid, to estimate the sulphur present as pyrrhotite as accurately as possible. Authorities give no method to meet the conditions. After a careful investigation of the matter I have perfected the following method; I am indebted to Mr. Lucius Pitkin, of New York City, for some valuable suggestions. It is based on the fact that Fe_7S_8 is magnetic, pyrites being non-magnetic.

[1] *Ber. d. chem. Ges.*, 1882.

[2] This Journal, 13, 210.

Method.—After the ground sample has been passed through a sixty mesh seive, 13.74 grams are weighed and spread out upon a good-sized sheet of glazed paper. A magnet is passed through and over this several times, the magnetic portion being carefully separated from the magnet by first stroking suddenly the top of the magnet, which dislodges most of the mechanically admixed pyrites, and then, secondly, separating the magnetic portion by means of the armature and a brush. The process is carried out five or six times, enough separations having been made to have reasonably separated all the magnetic portion. This is then finely ground in an agate mortar and the sulphur estimated gravimetrically by oxidation with nitric and bromo-hydrochloric acids. The weight of barium sulphate obtained in grams is the percentage of sulphur present as pyrrhotite.

The accuracy of this method was proved by the following work:

A sample of ore containing a known percentage of pyrrhotite was obtained. It analyzed as follows:

	Per cent.
Total sulphur	35.07
" Iron	57.50
Oxygen as Fe_3O_4	4.26
Copper	0.25
Insoluble matter	2.78
	99.86

Sulphur present as		Fe_7S_8	24.14
Iron	"	" Fe_7S_8	36.96
"	"	" FeS_2	9.34
Sulphur	"	" FeS_2	10.68
Iron	"	" Fe_3O_4	11.20

A sample of pyrites containing no pyrrhotite nor magnetic portion was then obtained. To a definite portion of this I added enough of the ore containing pyrrhotite to give 1.20 per cent. of sulphur present as pyrrhotite in the mixture; *i. e.*, to fifty grams of the pyrites I added 2.63 grams of pyrrhotite ore, or

$$\frac{24.14 \times 2.63}{52.63} = 1.20 \text{ per cent. sulphur as } Fe_7S_8.$$

This mixture was then analyzed for sulphur present as pyr-

rhotite by the method described above, using different weights. Some of the results obtained are :

5.00 grams	gave	0.4120	barium sulphate	=	1.13	per cent.	sulphur	as	Fe_7S_8.
13.74	"	1.1300	"	=	1.13	"	"	"	Fe_7S_8.
25.00	"	2.1570	"	=	1.18	"	"	"	Fe_7S_8.

Others were equally concordant.

The method was also applied to the pyrrhotite, as mentioned above, using portions of one gram or one-half gram giving respectively 24.13 per cent. and 24.15 per cent. sulphur as Fe_7S_8.

This method is accurate to within two-tenths per cent. on ores containing much or little pyrrhotite. The ore must not be finer than that which will pass through a sixty mesh sieve; if it is, results will be unreliable.

Another method, which I used until the perfection of this one, is based upon the fact that Fe_7S_8 gives off hydrogen sulphide with dilute acid, whereas FeS_2 (pyrite) does not. This is reliable when no other sulphides are present, but as most pyrites contain blende the results are usually unreliable.

CLEVELAND, O.

DROWN'S METHOD OF DETERMINING SULPHUR IN PIG IRON.

BY GEORGE AUCHY.

Received February 26, 1896.

OF the various evolution methods of determining sulphur in pig iron, Drown's is perhaps the best. Methods in which the sulphur is precipitated in any other form but barium sulphate (cadmium sulphide for instance), are not so convenient for the reason that the sulphur in the graphitic residue must be determined as barium sulphate. A slight drawback, however, attaches to the method in that the evolution of the gas must not be allowed to proceed too rapidly, and it is an object of this note to point out that by the use of potassium hydroxide solution in conjunction with the potassium permanganate solution as an absorbent for the gas, this caution is made unnecessary, and the gas may be passed through the solution as rapidly as it is possible to make it do so, without danger of loss; a mixed solution of caustic potash and potassium permanganate possessing stronger oxidizing power, than a solution of the latter salt alone. For there is a tendency in such a mixture, even

when no reducing agent is present, to the liberation of an atom of oxygen and a reduction of the potassium permanganate to potassium manganate, by the union of a molecule of potash with a molecule of potassium permanganate.

$$K_2O.Mn_2O_7 + K_2O = 2K_2MnO_4 + O.$$

If a very large excess of caustic potash solution be added to a few drops of potassium permanganate solution, the reduction to green potassium manganate will be seen to take place immediately. But in a mixture of equal or nearly equal parts of the two solutions, the change is very slow and gradual, except a reducing agent be present.

Convenient proportions of the two solutions for use as an absorbent in the determination of sulphur in pig iron are obtained by using in each case six cc. of a caustic potash solution, made by dissolving six sticks of the solid hydroxide in 350 cc. water, and six cc. of a permanganate solution containing about ten grams of the crystallized salt to the liter of water.

These volumes of the two solutions are carefully withdrawn from the bottles containing them by pipettes, so as to avoid getting any of the sediment at the bottom of the bottle ; mixed in a small beaker, and drawn into a Troilius bulb, which is then connected with the evolution flask containing the drillings. The solution of the pig iron may be accomplished in five or ten minutes without any hydrogen sulphide passing through the caustic potash and permanganate solution unabsorbed. The purple color of the permanganate gradually changes to the green of the manganate, which latter solution is also a stronger oxidizing agent than permanganate.

Not an inconsiderable convenience also in the use of this mixed solution is in the fact that the oxide of manganese separating out does not adhere to the glass tenaciously, and may be washed out with water instead of requiring to be dissolved out by strong hydrochloric acid and added to the main solution.

The next step in Drown's method is getting the manganese in colorless solution preparatory to the precipitation by barium chloride. This is accomplished by evaporation to dryness with hydrochloric acid, and separation of silica ; or by adding enough hydrochloric acid to get the clear solution by the aid of heat, but

without the tedious evaporation to dryness, and afterwards neutralizing the excess of acid with ammonia. The writer would suggest the use of oxalic acid in connection with hydrochloric acid, as by its use the solution of the manganese oxides is effected almost instantaneously and without the use of an excess of hydrochloric acid, a very small amount of the latter sufficing, and the barium chloride precipitation may then at once take place.

In detail: Take 3.4335 grams of the pig-iron drillings in a sixteen-ounce gas flask and connect with the Troilius bulb containing the mixed solution of caustic potash and potassium permanganate, as described. Pour through the funnel tube dilute hydrochloric acid in not unnecessary amount, and bring quickly to a boil. Then push to a cooler part of the plate and aspirate air through. A convenient arrangement is to have a narrow upright board fastened to the desk, or on a stand next to the filter pump; on the other side of the board stands the iron plate. This upright board, standing edgewise to the plate, is provided with nails or hooks for the support of the Troilius bulbs which are hung one above the other. Three or four determinations can be carried on at once in this way with the greatest possible economy of desk room. The aspirating is done by the filter pump.

Transfer the contents of the Troilius bulb to a small beaker, washing out with water. Filter the solution in the evolution flask through a ribbed filter and wash with hot water. Then punch a hole in the paper and wash the graphite and silica into an evaporating dish. Evaporate to dryness. Add thirty cc. aqua regia. Evaporate to dryness. When dry, add eight to ten cc. dilute hydrochloric acid. Heat, dilute with hot water and filter into the solution washed out of the Troilius bulb. Bring this solution then to a boil, add enough oxalic acid to clear the solution, (a very little will suffice), then five cc. barium chloride solution and boil about an hour. Allow to stand over night. The barium sulphate found, multiplied by four, will give the percentage of sulphur in the pig.

Caustic potash solution always contains considerable amounts of dissolved silica (for instance, in six cc. the amount used in a determination was found to be 0.0051 gram). But it is not

necessary to separate it, as a recent writer in the *Chemical News* has shown that precipitated barium sulphate is not contaminated by silica in solution, and the following experiments also show it. In these experiments a standard solution of sulphuric acid was used; mixed in each case with the amounts of caustic potash solution, and permanganate solution that are used in a regular determination. Instead of using ten cc. of hydrochloric acid, however, twenty cc. were used, but afterwards made alkaline with ammonia, then hydrochloric acid added drop by drop till just acid again, and the solution filtered from the alumina remaining undissolved. Then precipitated by barium chloride. Also the excess of oxalic acid used to bring the manganese oxides into solution was destroyed by permanganate solution before the neutralization and precipitation and the slight excess of permanganate by a piece of fine iron wire and stirring. The barium sulphate found was, for convenience in each case, calculated as though the usual amount of drillings had been taken, and a regular determination had been made.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.237	0.238
" 2	0.121	0.119
" 3	0.057	0.057
" 4	0.029	0.033

To note the effect of precipitating in a strongly acid solution, and one which therefore required no filtration from alumina before precipitating, the following tests were made as before, but with ammonia added to leave five cc. of free hydrochloric acid at time of precipitation (excess of oxalic acid again destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.121	0.112
" 2	0.121	0.114
" 3	0.237	0.234
" 4	0.057	0.054
" 5	0.029	0.029
" 6	0.014	0.010
" 7	0.029	0.028
" 8	0.029	0.026
" 9	0.014	0.010

These results show a very marked tendency to lowness. The following were then made, using ten cc. of hydrochloric acid for solution of the manganese oxides (together with oxalic acid, the excess of the latter, however, afterward destroyed by adding permanganate solution), and without any after neutralization with ammonia whatever, the solution therefore containing *over* five cc. of free acid, but no ammonium chloride.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.014	0.014
" 2	0.029	0.029
" 3	0.121	0.115

At this point it was thought well to also try the effect of oxalic acid upon the precipitation. It was feared it might have a solvent action upon the barium sulphate, especially in strongly acid solutions. In other respects the conditions were the same as in the series immediately preceding—ten cc. hydrochloric acid, no ammonia, etc., but excess of oxalic acid *not* destroyed.

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.014	0.014
" 2	0.029	0.029
" 3	0.121	0.118
" 4	0.029	0.029
" 5	0.060	0.059
" 6	0.090	0.090
" 7	0.045	0.046
" 8	0.060	0.060
" 9	0.090	0.090
" 10	0.029	0.029
" 11	0.014	0.014
" 12	0.121	0.119
" 13	0.237	0.239

From these results it would seem that the oxalic acid helped rather than hindered the precipitation of barium sulphate.

To see if there was any tendency of barium oxalate to precipitate, a test was made under conditions identical with No. 13, except that the solution was neutralized with ammonia till merely faintly acid before precipitating. Result 0.239 per cent., or just the same as in the strongly acid test. Showing no tendency of barium oxalate to precipitate.

Again, in standard solution equivalent to 0.121 per cent. taken, ten cc. hydrochloric acid added, brought to a boil, and precipitated with barium chloride. Result 0.119 per cent. Then the test repeated twice with addition of oxalic acid. Results, No. 1, 0.120 per cent., No. 2, 0.120 per cent.

Thinking perhaps good results could also be obtained by allowing the precipitated barium sulphate to stand only one hour before filtration, the following tests were made (ten cc. hydrochloric acid, no ammonia, excess of oxalic acid not destroyed).

	Sulphur taken. Per cent.	Sulphur found. Per cent.
No. 1	0.029	0.024
" 2	0.014	0.007
" 3	0.029	0.023
" 4	0.121	0.115
" 5	0.060	0.056
" 6	0.045	0.041

Showing that one hour's standing is not sufficient. But the loss seems so uniform that in cases of hurry it would be perhaps safe to allow only one hour for standing, making afterward a correction in the result of 0.005 per cent.

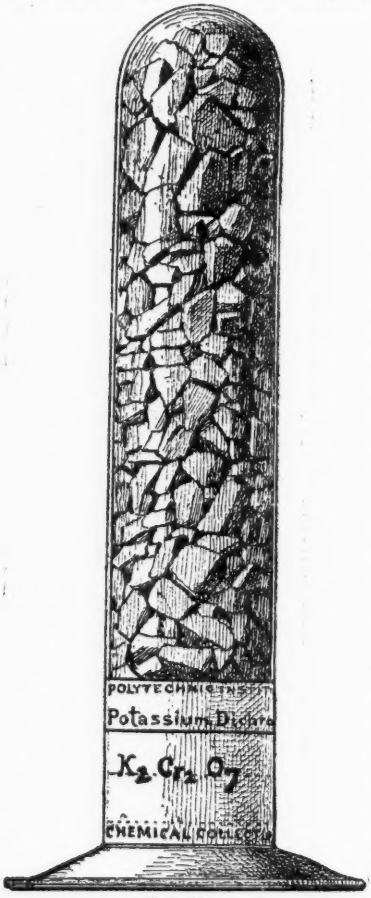
It is important to make a blank or dummy test with the reagents used. In this test use double the reagents and precipitate in nearly neutral solution.

In the regular determinations also precipitations may of course take place in nearly neutral solutions if so desired, and as is usually recommended. The results of the second series, however, may perhaps be taken as a warning against the presence of ammonium chloride in *strongly* acid solutions, and the ammonia should therefore be added to near neutralization if used at all.

In filtering off the barium sulphate it is not advisable to use a rapid filtering funnel, as barium sulphate equal to 0.002 or 0.003 per cent. is more than likely to pass through the filter paper and escape notice in the filtrate, except the liquid be stirred in such a way as to collect it together in the middle of the bottom of the beaker. When hydrochloric acid is spoken of in this article the dilute acid (equal parts water and acid) is meant.

NOTE.

A New Specimen Bottle.[1]—There are several reasons why glass-stoppered bottles are well adapted for small specimens. The neck and stopper form an awkward cover looking to the specimen. The neck is usually too small in proportion to the width of the bottle, and as a specimen is not intended to be taken out of its receptacle, the stopper and ground neck are inappropriate. But the chief objection to their use is their cost.



FULL SIZE.

The form which I have found to be very practical consists of a tube with a rounded top provided with a flanged base. This form is pleasing to the eye, exhibits the whole of the specimen, is not easily upset, is air- and moisture-tight, and is low priced.

In filling the tube, it is inverted, and when enough of the specimen has been put in, a cylindrical (not conical cork) is pushed in. When the specimen does not pack, or when but few crystals are placed in the tube, it is well to paste a disk of white paper in the top of the cork, so as to conceal it from sight. In the case of colorless crystals, glazed black paper gives a better effect. The

[1] Read before the New York Section, October 4, 1895.

cork should be driven in so as to leave about one-sixteenth of an inch space below the jointure of the tube and the flange. Melted paraffin is then poured in. A layer a quarter of an inch thick is quite enough to exclude air and moisture and to hermetically seal the tube. If desirable, the whole space of the base may be filled with paraffin, and, when cool, the wax may be pared down flat with a knife long enough to touch both sides. The addition of a little lampblack to the paraffin makes a better effect. The label is then put on. It should be long enough to give a slight lap and wide enough to cover the cork. The top of the cork should be just level with the edge of the label. The inside of the base flange may be painted with black varnish, or it may be made of black or colored glass.

The flanged base prevents the tubes from touching each other, and thus shows off the samples very effectively. It is well to arrange the shelves in stairs. The steps may be three inches wide and two and a half inches high. The rows should be alternate, so that the labels of each row but the first may be seen between the tubes of the row in front of it.

When a small amount or a single crystal of a specimen is to be exhibited, a good effect can be produced by thrusting a copper wire into the cork and twisting the other end into a circle about half an inch in diameter. On this is placed a three-fourths of an inch watch glass, and in this the specimen. The stalk of the support should be about two inches long. Other modifications will naturally occur to any one.

As the operations involved in making these specimens are few and simple, their cost is low in comparison with the ground glass-stoppered bottles. Whitall and Tatum make the size represented in the cut for $7.00 a gross in four gross lots, which is a shade less than five cents a piece. Larger or smaller sizes can be furnished at proportional prices.

PETER T. AUSTEN.

BROOKLYN POLYTECHNIC INSTITUTE,
January 15, 1896.

BOOKS RECEIVED.

The Smithsonian Institution: Its Origin, Growth, and Activities. By Prof. Henry Carrington Bolton, Ph.D. New York: D. Appleton & Co. 30 pp.

Handbook of the Bio-Chemical Laboratory. By John A. Mandel. New York: John Wiley & Sons. v, 101 pp. Price $1.50.

Bulletin No. 28. An Important Elm Insect. Reno, Nev.: Agricultural Experiment Station of the Nevada State University. November, 1895. 8 pp.

Bulletin No. 29. The San Jose Scale. Reno, Nev.: Agricultural Experiment Station of the Nevada State University. December, 1895. 8 pp.

Bulletin No. 121. Hillside Terraces or Ditches. Raleigh, N. C.: North Carolina Agricultural Experiment Station. October, 1895. 8 pp.

Bulletin No. 125. Forage Grasses and Hay-Making. I. Tests of Forage Grasses. II. The Formation and Care of Grass Lands. III. Haying Tools and Hay-Making. Raleigh, N. C.: North Carolina Agricultural Experiment Station. January 15, 1895. 41 pp.

Ueber Reindarstellung der Gährungsmilchsäure mit einleitenden Versuchen über Destillation in Vakuum der Quecksilberluftpumpe. Dissertation by Wilhelm A. Dyes, Ph.D. 1895. 44 pp.

ERRATA.

On page 223 (March number) under solution number 3, instead of

Water ..... 115 cc.

read

Water ..... 190 cc.

and instead of

Phosphoric acid 1.40 sp. gr..... 315 cc.

read

Phosphoric acid 1.40 sp. gr..... 340 cc.